



## Synthesis of Polypropylene Fiber / Hydrated Iron Oxide Nanocomposite Adsorbent

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Composite adsorbent based on the polypropylene fibers with chemically bound nanoparticles of hydrated iron (III) oxide were synthesized by two-stage experiment: radiation-induced graft polymerization of acrylic acid onto the surface of polypropylene fibers followed by the in-situ formation of hydrated iron oxide nanoparticles and their stabilization on the fibers' surface within the grafted layer. SEM and XRD investigations revealed a compact homogeneous layer of amorphous nanoaggregates (70-100 nm) formed by iron hydroxide on the fibers' surface. The synthesized nanocomposite fibers were stable in the aggressive medium for a long time and exhibited good adsorption properties for uranyl ions.

**Keywords:** Polypropylene fibers, Radiation-induced graft polymerization, Acrylic acid, Hydrated iron oxide, Nanoparticles, Uranium adsorption.

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### 1. INTRODUCTION

Polypropylene (PP) fibers and non-woven fabrics are widely used in sorption processes as an adsorbing filtration material. They are attractive because of their low cost, good mechanical strength, chemical and thermal resistance of the PP base and high specific surface of fibrous structure. The range of possible applications of these materials can be extended by modification of the hydrophobic, chemically inert PP base. Graft polymerization technologies and, in particular, radiation-induced graft polymerization have become increasingly used for this purpose [1]. This method allows grafting of nano- or microchains of a vinyl monomer with a desired functional group onto the surface of an inert polymeric base, ensuring control over the length and density of the grafted chains. The resulted material consists of two parts: the polymeric base and the chemically bound chains with functional groups (ion-exchange or chelating), and so it can be used as polymer adsorbent.

In the past decades, fibrous polymer adsorbents have been considered as potential alternative to granular ion exchange resins because of their high specific surface, high ion exchange capacity, and high adsorption speed [2-4]. Numerous adsorbents on the base of PP fibers and fabrics have been synthesized by radiation graft polymerization method, but only a few of them could be adjusted for selective removal of pollutants from water effluents because of limited variety of available functional groups.

In recent years, composite adsorbents (polymer/inorganic nanoparticles) have been developed as a new class of adsorption materials. They were fabricated mostly by the in-situ formation and/or incorporation of inorganic nanoparticles into voids of macroporous polymer beads [5-7].

Although fibrous polymers with ion-exchange groups could be a hosting matrix for fabrication of the composite adsorbents, there are only several publications on this theme [8, 9].

The present investigation has been undertaken for two reasons: (i) to develop the synthesis route for fabrication of composite adsorbent with nanoparticles of hydrated iron (III) oxide (HIO) based on polypropylene fibers; (ii) to examine the obtained nanocomposite fibers for removal of uranyl ions from the model solutions in batch process.

### 2. EXPERIMENTAL SECTION

#### 2.1 Preparation of PP-hydrated Iron Oxide Nanocomposite Fibers

Polypropylene fibers, available from Saehan Filter Co Ltd, were used for synthesis of nanocomposite adsorbent. All chemicals were of analytical grade.

The nanocomposite fibers were synthesized through the two-stage experiment. At the first stage the chemically inert PP fibers were activated through radiation-induced graft polymerization of acrylic acid (AA) for introduction of chemically active carboxyl groups on the PP fibers' surface.

The second stage consisted of the following three steps: Ion-exchange (PP fibers with grafted polyacrylic acid (PAA) chains (PP-g-PAA fibers) were immersed in 0.1 M FeCl<sub>3</sub> solution for 12 h); In-situ formation of hydrated iron oxide nanoparticles (PP-g-PAA fibers with loaded Fe<sup>3+</sup> ions were put into NaOH solution with pH 9-10 for 15 min); Rinsing and thermal treatment (the resulting composite fibers were washed with deionized water till neutral pH and then dried at 60 °C in oven for 24 h).

#### 2.2 Characterization

The morphology of the PP fibers before and after modification was recorded by a Hitachi S-4200 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. XRD patterns of the powdered samples were recorded on a Dron-3 diffractometer using Cu-K<sub>α</sub> radiation.

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Phase structure and Fe (III) content of the HIO were estimated by "hydroxylamine test". The known amount of the composite material was solved in hydroxylamine - hydrochloride solution (0.25 M : 0.25 M) at 50 °C for 6 h [10]. Iron concentration in the resulting solution was measured using an atomic absorption spectrophotometer model AA-8500 (Nippon Jarrell-Ash Co. Ltd., Kyoto, Japan).

Stability of the synthesized composite fibers in acid and basic water solutions was tested at room temperature. Composite fibers (0.1g) were placed in the flasks with 10 ml of solution with different pH values and after required time the residual solutions were tested for the iron content.

Adsorption experiments were carried out in batch mode using synthetic, single ion solutions. The uranium concentration in the solution was measured by X-ray fluorescence analysis (AUF-101 laser fluorometer "Angara", Russia). All the experiments were performed in duplicate.

For desorption studies the spent composite fibers with the known amount of absorbed uranium were gently washed with distilled water three times for 2 min to remove the unadsorbed uranium ions and dried to remove water. Then the adsorbent was mixed with 20 ml of eluting solution and agitated for required time. The desorbed uranium was estimated in the solution as before.

### 3. RESULTS AND DISCUSSION

#### 3.1 Preparation of Polypropylene / Hydrated Iron Oxide Nanocomposite Fibers

The composite PP-HIO fibers were synthesized by two-stage experiment: radiation-induced graft polymerization of acrylic acid followed by in-situ formation of iron hydroxide colloidal particles and their deposition on the fiber surface within the grafted layer.

The first stage, which resulted in synthesis of PP fibers with grafted polyacrylic acid chains (PP-g-PAA) with a wide spectrum of carboxylic group density, was examined previously [11]. To prepare nanocomposite adsorbent the PP-g-PAA samples 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 second stage involved the in-situ formation of HIO nanoparticles through the loading of carboxylic groups of grafted PAA chains with Fe<sup>3+</sup> ions and subsequent precipitation of iron hydroxide on the fiber surface in the basic medium (pH ~ 9-10). The latter process, it seems, took place inside of the grafted chains, because no red precipitation was observed on the bottom of the flask with PP-g-PAA(Fe) sample after adding the basic solution. Thus, we can presume that grafted chains served as nanorectors for the formation and stabilization of HIO nanoparticles.

As a result of the above two-stage experiment the composite material based on the polypropylene fibers with surface loaded hydrated iron oxide nanoparticles was obtained.

#### 3.2 Characterization of Polypropylene / Hydrated Iron Nanocomposite Fibers

Figure 1 shows SEM images of the initial and grafted

PP fibers with surface loaded HIO nanoparticles. The initial PP fibers (Fig.1a) have a smooth surface and a diameter of  $20 \pm 5 \mu\text{m}$ . After grafting and hydrated iron oxide deposition, the fibers' diameter increased to  $25 \pm 5 \mu\text{m}$  and their initially cream color changed to reddish-brown. One can see that surface loaded HIO formed a homogeneous layer on the PP fibers' surface (Fig.1b). The SEM image at a higher magnification (Fig. 1c) shows a specific microstructure of the HIO layer. This layer consists of the nanosized HIO aggregates (70-100 nm) which are rather regular in shape and closely fit one to another forming a compact texture.

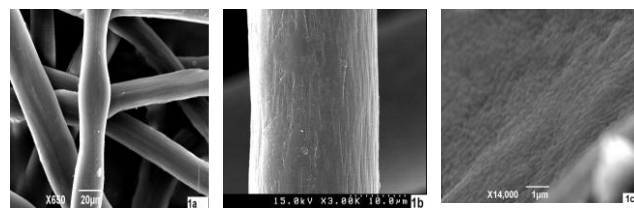


Fig. 1 – SEM images of the initial PP fibers (1a) and grafted PP fibers with surface loaded hydrated iron oxide nanoparticles (1b and 1c).

#### 3.3 Phase Composition and Fe Content of the HIO Layer

The HIO layer phase structure depends on the experimental conditions during the second experimental step. When precipitation of iron hydroxides proceeds at room temperature and pH is less than 10 following by the mild thermal treatment, the HIO of amorphous structure should be obtained [12].

The XRD diffraction spectra (Fig. 2) of the PP-HIO nanocomposite fibers implied that HIO nanoparticles loaded on the fibers' surface have amorphous structure.

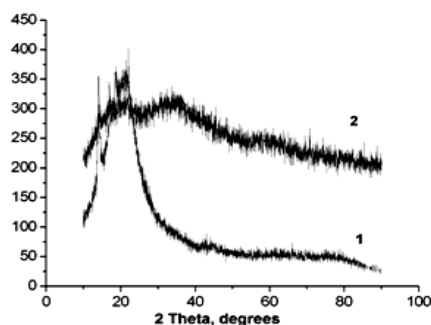
The amorphous structure of the hydrated iron oxide layer formed on the PP fibers' surface was confirmed by the "hydroxylamine test". This test is widely used for separation of amorphous (or poorly crystalline) iron (III) oxides and crystalline ones in soils, because the hydroxylamine - hydrochloride solution readily dissolves poorly crystalline and amorphous iron (III) oxides, while minimizing the attack of the crystalline phase (< 1%) [10]. After treatment the composite PP-HIO fibers in the hydroxylamine-hydrochloride solution the fibers completely lost the HIO layer and their reddish-brown colour changed back to the initial cream one. The composite PP-HIO fibers were calculated to contain about 5% of Fe. It means that almost all Fe<sup>3+</sup> ions loaded on the PP-g-PAA fibers were deposited as hydrated iron oxide nanoparticles within the grafted PAA chains during the second stage of our synthesis.

Stability of the synthesized composite fibers in acid and basic solutions was tested at room temperature and results are shown in Table 1. One can see that composite fibers are stable in aggressive medium and they negligibly release Fe into the contacting solution. It follows from table 1 that less than 2 % of Fe was released from HIO layer after 42 days at pH 2.

#### 3.4 Uranyl adsorption studies

In order to determine the adsorption properties of

the synthesized composite fibers a set of batch experiments towards uranyl ions uptake from the water solutions was performed. It is known, that at low pH the uranyl ions are of dominant ionic form in the water solution for a wide uranium concentration range, while other hydrolyzed uranium ions appear in the solution with increasing pH to the neutral value. Therefore, all experiments were conducted at pH ~ 2.5.

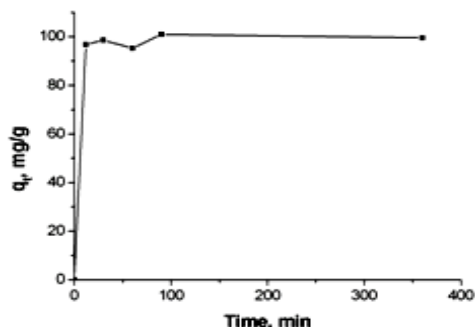


**Fig. 2** – XRD spectra of PP (1) and PP- hydrated iron oxide nanocomposite fibers (2)

**Table 1** – Stability of nanocomposite PP-HIO fibers in water solutions with pH

pH	Contact time, days	Concentration of Fe in solution, mg/L
2,8	1	0,9
2,0	42	9,0
5,1	1	0,6
8,3	1	0,3
10,5	1	0,1

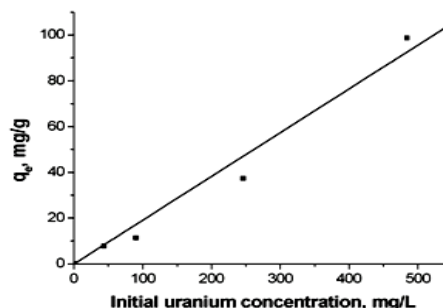
The effect of contact time was studied at the initial uranium concentration of 484 mg/L (Fig.3). It is observed that the adsorption equilibrium was attained fast in about 20-30 min. The complete uptake of uranyl ions (99.9 %) proceeded within this time period. The fast adsorption rate suggests that the adsorbing groups are readily available and easily accessible probably because of the large surface area and big density of reactive sites on the HIO nanoparticles.



**Fig. 3** – Effect of contact time on the adsorption of uranyl ions ( $q_e$ ) by polypropylene/ hydrated iron oxide nanocomposite fibers. Initial uranium concentration 484 mg/L; initial pH 2.5, room temperature, periodical shaking

The effect of initial uranium concentration on the equilibrium adsorption capacity of the synthesized samples (equilibrium time of 24 h was taken for all samples) was investigated and results are shown in Fig. 4. It is

evident from the figure, that the amount of uranium adsorbed increases linear from 0.2 to 98.7 mg/g with the increase in initial concentration from 0.5 to 484 mg/L. The obtained results indicate that an increase in initial uranium concentration enhances the adsorption uptake of uranyl ions by the synthesized adsorbent.



**Fig. 4** – Effect of initial uranium concentration on the adsorption of uranyl ions by polypropylene/ hydrated iron oxide nanocomposite fibers

The obtained results on sorption properties demonstrate that synthesized fibrous PP-HIO nanocomposite adsorbent has a high potential to be used in removal of uranium ions from wastewaters. However, the further studies are needed to be carried out.

In order to regenerate the synthesized adsorbent so that it can be used again, the desorption experiments were carried out by using four eluting solutions – distilled water, 1 M sodium acetate, 0.5 M sodium carbonate, and hydroxylamine - hydrochloride solution. As it follows from Table 2, neither water, nor sodium acetate is effective eluting solution that points on the chemical bonds between HIO and uranyl ions. In spite of the fact that recovery of uranyl ions by sodium carbonate in 24 hours was 68,7%, the maximum recovery (100%) was achieved by increasing time of desorption to 36 hours. The high efficiency of recovery by sodium carbonate can be explained by formation of stable uranium-carbonate complexes. The hydroxylamine - hydrochloride reagent effectively transfers uranyl ions into the solution due to the complete dissolution of HIO layer.

Thus, when applying 0.5 M sodium carbonate as eluting solution it is possible to desorb uranium completely and thereby regenerate the PP-HIO nanocomposite adsorbent for its reuse.

**Table 2** – Results of desorption experiment

Elution solution	Contact time, h	Desorption, %
0.5 M sodium carbonate	24	68,7
0.5 M sodium carbonate	36	100,0
Distillated water	24	0,0
1 M sodium acetate	24	0,1
Hydroxylamine-hydrochloride solution	24	100,0

#### 4. CONCLUSIONS

1. Composite adsorbent based on polypropylene fibers with chemically bound nanoparticles of hydrated iron (III) oxide were synthesized by two-stage experiment: radiation-induced graft polymerization of acrylic acid onto surface of polypropylene fibers followed by in-

situ formation of hydrated iron oxide nanoparticles and their stabilization on the fibers' surface within the grafted layer.

2. SEM and XRD investigations revealed the compact homogeneous layer of amorphous nanoaggregates (70-100 nm) formed by iron hydroxide on the fibers' surface.

3. The synthesized nanocomposite fibers were stable

in the aggressive medium for a long time and exhibited good adsorption properties for uranyl ions.

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