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FIBROUS CATALYSTS AND SORBENTS FOR DESTRUCTION OF TOXIC ORGANIC POLLUTANTS IN WASTWATERS

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Abstract. Methods of production of a fibrous catalyst and ion-exchange sorbent were developed and patented at St.-Petersburg State University of Technology and Design (SUTD). A knitted fabric (mesh) was used as catalyst as well as sorbent support. The knitted structure of the support provides an extensive mass- and heat- transfer area for the catalyst. The mesh consisted of polypropylene monothread (58-60%) and polyacrylonitrile complex thread (40-42%) with linear densities of 64.3 and 27.2 tex respectively. PAN thread is synthesized from: acrylonitrile (92.3 %), methylmetacrylate (6.2 %) and itaconic acid (1.5 %). Polypropylene monothread gives incompressibility and flexibility to the mesh, so that the catalyst/fibrous sorbent could be folded in a variety of shapes to fit the reactor.

The production of PAN fibrous catalyst was performed using hot aqueous solution of hydrazine and hydroxylamine in three steps. The modification results in formation of functional groups that can strongly ligate a multivalent metal (such as iron) to the fibre.

The activity of the developed catalyst was investigated towards degradation of an anionic detergent (Sulfonol-NP). The experiments were performed at a room temperature and pH=3 using oxygen of air and hydrogen peroxide as oxidants. The greatest destruction degree of Sulfonol was 87-90%. Activation energy of Sulfonol catalytic oxidation calculated using the experimental data is 32 kJ/mol.

The other modification of PAN includes treatment of PAN/PP mesh with aqueous mixtures of hydroxylamine and ethylenediamine and produces a ion-exchange sorbent. Identification of functional groups of the modified PAN was performed by means of FTIR spectroscopy. Formation of amino-, amido- carboxilate groups was detected. The modified PAN fibre is an ampholyte. Depending on the modification parameters (pH of modification solution and duration of the process) cation and anion exchange capacities of the sorbent are 2.7 - 3.4 and 0.7 - 1.2 mmol/g respectively.

Keywords: polyacrylonitrile, fibrous ion-exchange sorbent, fibrous catalyst, acid dyes, surfactants, oxidation

1. Introduction

Polyacrylonitrile (PAN) fibre is widely used as a support for ion-exchange (Mubarakshin 1979; Ananyeva *et al*. 1987) and chelating sorbents (Chang *et al.* 1994; Nemilova *et al*. 1996; Liu *et al.* 1999; Dong *et al.* 2004) as well as catalysts (Ishtchenko 2002; Petrov 2000). A number of modification techniques have been developed for the co-polymer of acrylonitrile and methylmethacrylate (Barash *et al.* 1988) and for the tri-polymer which contains (in addition to acrylonitrile and methylmethacrylate) itaconic acid or vinylsulphonate (Kulinsky *et al*. 1975; Todorov *et al.* 1996).

Modification of PAN fibre can be performed by non-reagent or reagent techniques. Thus, non-reagent methods of PAN modification usually include thermal treatment of the fibre and are used to produce carbon fibres. Actually PAN fibres are the most widely used precursors in the production of carbon fibres. Generally the process of carbon fibre production includes stablisation treatment at 200–300^{0}C as a first strep and second step is carbonization at high temperature (≥ 1000^{0}C). The thermal treatment results in the formation of cyclic structures (Romanova 1985; Wang *et al*. 1996).

Reagent modification techniques which have previously been developed include treatment of the fibre with either aqueous or non-aqueous solutions of hydrazine, hydroxylamine and a variety of organic amines, both low molecular weight (ethylenediamine, monoethanolamine, EDTA) and polymeric (e.g. polyethanolpolyamine). The interactions between nitrile group and these compounds are complicated and the exact structure of the resultant functional groups has not been identified. There have been a number of attempts to characterize the structure of the modified fibre by means of chemical analysis, e.g. Kjeldal technique (Kudryavtsev *et al.* 1965; Todorov *et al*. 1996) as well as spectroscopic (FT-IR, UV) (Chang *et al*. 1994) and thermo-gravimetric

(TGA and DTA) techniques. The investigations suggested a variety of possible reactions between −C≡N group and the modification reagents. Functional groups of itaconic acid and methylmethacrylate also undergo reaction with hydrazine and hydroxylamine.

Chelating and ion-exchange fibres produced from modified PAN fibre have been widely used for removal of toxic heavy metals (Ni, Co, Pb, Zn, Cu etc.) from aqueous solutions (Chang *et al.* 1994; Dong *et al.* 2004). Anion exchange fibres VION were used for hydrogen sulphide removal from gaseous wastes (for example, emissions of viscose production).

The catalyst developed at SUTD was successfully used for decolourisation of simulated effluents of an anthraquinone dye Acid Blue 45 and Natural Red (Ishtchenko 2002) in acidic media, oxidation of phenol in aqueous solutions as well as decolourisation of real textile wastewater originated from William Baker Ltd, Leicester, UK. A slightly different modification (Petrov 2000) produced a catalyst which was used for oxidation of sulfides in real tannery effluents.

2. Experimental Techniques

2.1. Support for the fibrous sorbent and catalyst

As a sorbent and a catalyst support a knitted fabric (mesh) produced using a Raschel knitting machine (PAP, USA) was used. The mesh consisted of polypropylene (PP) monothread (58-60% w/w) and polyacrylonitrile (PAN) complex thread (40-42%, w/w). PAN thread was synthesized from: acrylonitrile (92.3 %), methylmetacrylate (6.2 %) and itaconic acid (1.5 %). Linear densities of PP monothread and PAN complex thread were 64.3 and 27.2 tex respectively. The PAN/PP mesh was produced at St.-Petersburg State University of Technology and Design.

2.2. Reagents

All reagents used in the research were analytically grade. Distilled water was used for making up all solutions as well as for washing the mesh between and after modification steps.

Modification reagents, hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, 99% purity, A.S.C. reagent, purchased from Sigma-Aldrich) and ethylenediamine (NH_2-CH_2-CH_2-NH_2, d^{20}=0.898 g/cm^3, 99% purity, A. S. C. reagent, purchased from Alfa-Aesar) were used as obtained.

Sodium hydroxide (97% purity, A.C.S reagent, purchased from Sigma-Aldrich*)* was used for adjustment of the pH of modification solution to the needed level.

An anthraquinone dye Acid Blue 45 ($C_{14}H_8O_{10}N_2S_2Na_2$, M = 474 g/mol, λ_{max} = 595 nm, dye content 50% purchased from Aldrich*)* was used for the investigation of sorption properties of the modified PAN fibre. The dye was used as obtained, without further purification.

2.3. Methods

The modified PAN fibre was characterised by means of Fourier Transform Infra-Red Attenuated Total Reflection Spectrometer technique (FTIR-ATR) as well as Electron Scanning Microscopy and Energy Dispersive X-ray Detection (SEM/EDX).

FTIR-ATR spectra were obtained using a Spectrum One FTIR Spectrometer (Perkin Elmer) equipped with Universal ATR Sampling Accessory (Perkin Elmer). The machine was operated by Spectrum Version 5.3 computer software. Spectra were registered in the wavenumber region of 4000 – 500 cm^{-1}. Samples for FTIR-ATR analysis were complex threads of the initial (i.e. non-modified) and modified PAN threads.

Microphotographs of modified PAN threads and EDX spectra of iron distribution were obtained at St-Petersburg State University of Chemical Technology. The microphotographs of the PAN fibre cross sections were prepared as slices for the analysis by means of JSM-35CF Scanning Electronic Microscope (JEOL). The parameters of SEM analysis were as follows: voltage 25 keV, probe current 6×10^{-6} A.

The cross-sections of the initial and modified and impregnated PAN mesh for SEM were prepared for the analysis by means of equipment purchased from Buehler (IsoMet Low Speed Saw and MiniMet 1000 Polisher) and all chemicals for sample preparation were also purchased from Buehler.

Initial and residual concentration of Acid Blue 45 in the solution as well as the dye UV/VIS spectrum were obtained spectrophotometrically by means of UV1 UV-Visible Spectrometer v1.08 (Unicam). The UV/VIS readings were taken using 10 mm quartz cells. Concentration of Acid Blue 45 in the solution was determined using a calibration graph plotted as D = f(C) in the concentration range of 0.5 – 10 mg/L. The absorbance readings were taken at λ = 595 nm.

Initial and residual concentration of the surfactant Sulfonol-NP were determined spectrophotometrically using a standardized technique described elsewhere (Lurye 1971).

2.4. Preparation of the fibrous sorbent

Modification of PAN/PP knitted mesh was carried out with aqueous solutions of hydroxylamine hydrochloride and ethylenediamine. Modification procedure is described in detail elsewhere (Orlova 2010). Molar ratio between ethylenediamine and hydroxylamine was 0.48 mol/mol. For the investigation of the effect of modification parameters on the structure and properties of the resultant PAN fibrous sorbent pH of modification solution varied from 7.5 to 9.5 and duration of the modification varied from 30 to 120 minutes.

The modification solution was prepared using distilled water. pH of the modification solution was adjusted to the desired level (7.5–9.5) using NaOH pellets, pH control was carried out by means of Conductivity/pH meter Jenway 4334.

2.5. Preparation of fibrous catalyst

PAN/PP mesh was treated with hot aqueous solution of hydrazine and hydroxylamine. Treated mesh was washed with distilled water and impregnated with a solution of multivalent metal (iron). The modification procedure is described in detail elsewhere (Vitkovskaya and Petrov 2005).

2.6 Oxidation of Sulfonol-NP

Oxidation of a surfactant Sulfonol-NP was performed in a batch mode using a 300 mL glass reactor equipped with a gas-distributing tube. Hydrogen peroxide and bubbled air were used as oxidants. Dose of hydrogen peroxide was 350 mg/L, bubbled air supply was 5 L/min. The oxidation experiments were performed at a room temperature (25^{0}C), pH of Sulfonol solution was 3.

3. Results and Discussion

3.1. Fibrous Sorbent

Due to chemical structure of modification reagents (hydroxylamine and ethylenedyamine) and modification conditions (pH of modification solution varied in the range from 7.5 to 9.5) the modified PAN fibre has both cation-exchange (carboxylate) groups and anion-exchange groups (amino groups).

The latter are protonated in acidic media to give –NH_3^+ groups which in their turn can bind negative charged ions, for example anions of acid dyes. Thus, PAN fibres treated with modification solutions of hydrazine, hydroxylamine, and different amines (ethylenediamine, polyethylene-polyamine etc.) are usually ampholytes unless modification is performed under specific conditions, e.g. in non-aqueous modification solution (Nemilova *et al,* 1996) or in vapour (Dragan *et al*, 2005).

In our research, functional groups of the original and modified PAN were identified by comparison of the obtained infrared spectra to those given in the literature (Kuptsov and Zhizhin 2001). FTIR-ATR spectrum of the modified PAN fibre scanned from the fibre surface (Figure 2) shows that –C≡N peak at 2243 cm^{-1} disappears completely after modification of polyacrylonitrile at pH=7.5, i.e. the process leads to the full conversion of surface nitrile groups. The strong broad band in the region of 3000-3600 cm^{-1} indicates the formation of hydroxyl- and amino groups. New peaks appear at 1636 cm^{-1} (C=O stretching vibration group in amides), 1380 cm^{-1} (C=O symmetric stretching vibration in carboxylate groups) and 920 cm^{-1} (N – O stretching vibration).

It can be seen from the Figure 3 that on the FTIR-ATR spectra of PAN modified at higher pH levels (8.5 and 9.5) the adsorption band at 3000-3600 cm^{-1} becomes even broader and more intense. This phenomenon can be attributed to the formation of –OH and – NH_2 groups due the hydrolysis of –C≡N group and its conversion to the carboxylate via the amide group. Formation of carboxylate groups can be illustrated by the reactions given below:

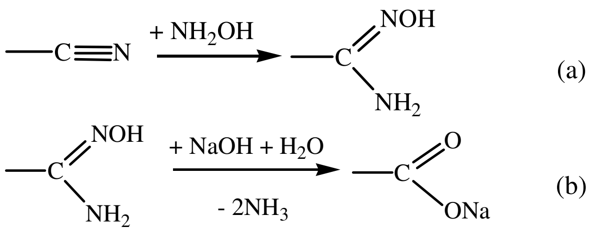


Fig 1. Reaction of the nitrile group of PAN with hydroxylamine to form amidoxime group (a) with further alkaline hydrolysis (b).

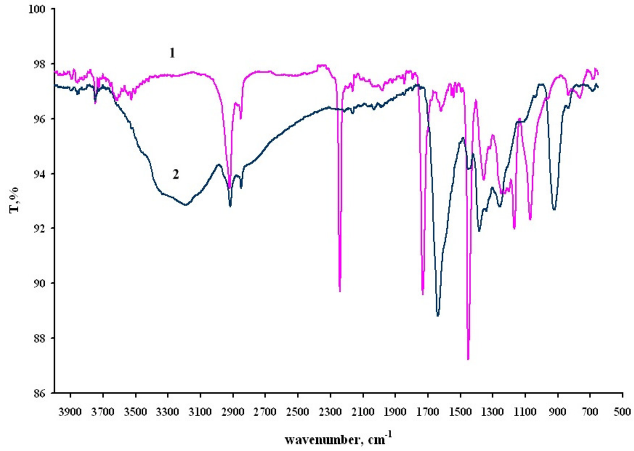


Fig 2. FTIR-ATR spectra of initial and modified PAN fibre, where: 1 – spectrum of the initial (non-modified) PAN fibre; 2 – spectrum of PAN fibre modified at pH = 7.5

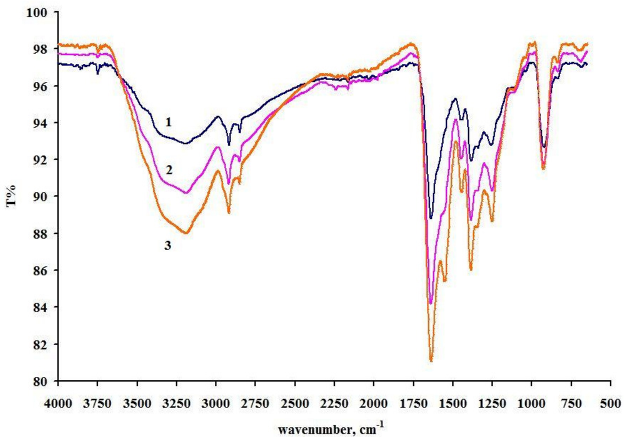


Fig 3. FTIR-ATR spectra of PAN fibre modified under varied pH, where: 1 – pH = 7.5; 2 – pH = 8.5; 3 – pH = 9.5

Generally infrared spectra of the modified PAN fibre are very similar to those known from previous modifications (Ishtchenko 2002). It can be concluded that modification of polyacrylonitrile fibre with hydroxylamine and ethylenediamine leads to the formation of carboxylate-, oxime, amino- and amido groups. Thus, the fibrous sorbent developed in our research has functional groups which introduce both cation and anion exchange properties to the fibre.

Conversion of the nitrile groups of PAN under action of aqueous modification solution of ethylenediamine and hydroxylamine proceeds mostly on the surface of the fibre. The process results in the formation of three-dimensional chemical structure which blocks further penetration of the fibre by the modification solution and diffusion of the reagents (hydroxylamine and ethylenediamine) into the polymer volume. This is supported by SEM/EDX data. Thus, microphotographs of the modified PAN fibre cross-sections (Figure 4) and EDX spectra of iron distribution show that iron is distributed mostly on the surface of the modified PAN fibre.

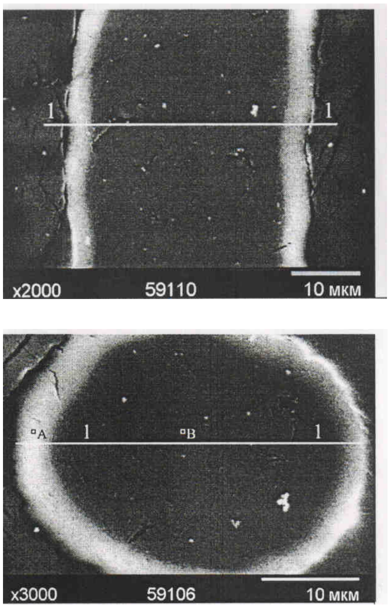


Fig 4. SEM photos of the modified PAN fibre impregnated with ferric chloride solution

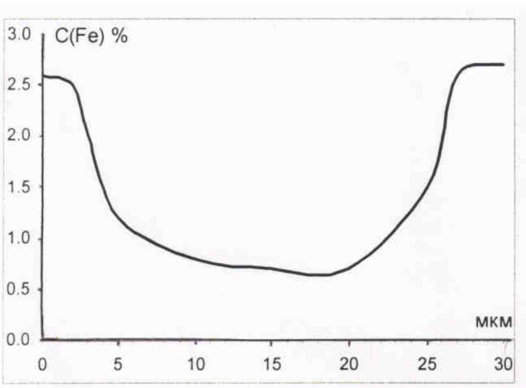


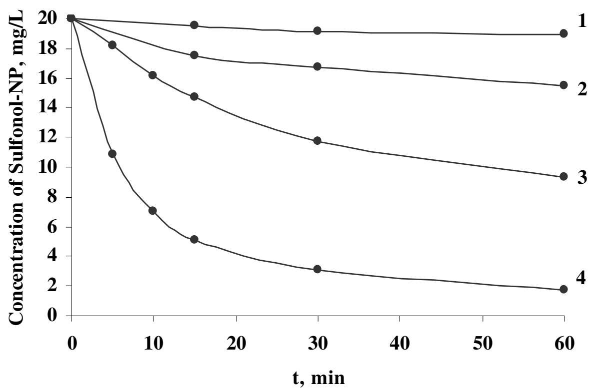
Fig 5. EDX Spectra of Iron Distribution

On Fig 4, pale regions of outer surface of the fibre are the range of iron penetration into PAN threads. According to EDX spectra presented in Fig 5, depth of iron penetration is approximately 5 µm, and concentration of iron on the surface of PAN treads is 2.3 – 2.5 % (w/w). SEM photographs on Figure 4 support FTIR-ATR data in that the modification of the nitrile group occurs mostly on the surface of the fibre. It is very likely that some crosslinking of polyacrylonitrile chains takes place which prevents penetration of fibre with modification solution.

Ion-exchange capacities of the resultant PAN fibrous sorbent as well as sorption activity of the fibre towards ions of different size (cations of Fe^{3+} and anions of acid dyes) were determined. Cation and anion exchange capacities of modified PAN were determined according a standardized titration technique in a batch mode. Depending on the modification parameters (pH of modification solution and duration of the process) cation and anion exchange capacities of the sorbent are 2.7 - 3.4 and 0.7 - 1.2 mmol/g respectively.

3.2. Fibrous Catalyst

The activity of the developed catalyst was investigated towards degradation of an anionic detergent (Sulfonol-NP). Effect of oxidants (oxygen of air and hydrogen peroxide) on the catalytic degradation of Sulfonol-NP was investigated. The experiments were performed at a room temperature in acidic media (pH=3). As can be seen from Figure 6, that non-catalytic degradation of Sulfonol-NP by oxygen of air (curve 1) as well as by hydrogen peroxide (curve 2) results in a fairly poor decrease in the surfactant concentration in the solution. Thus, degradation degree of Sulfonol-NP by oxygen of air comes to only 5.5% whereas catalytic degradation of the surfactant with oxygen and fibrous PAN catalyst (curve 3) results in 58.3% Sulfonol-NP removal. Usage of hydrogen peroxide alone (curve 2) results in 22.5% decrease in concentration of Sulfonol-NP and together with the catalyst degradation degree of Sulfonol-NP comes to 91.1%.



$[Sulfonol]_{initial}$ = 20 mg/L, pH = 3, t = 25^0C

Fig 6. Kinetic curve of Sulfonol-NP oxidation, where: 1 – blank experiment 1 (bubbled air supply 5 L/min, no H_2O_2, no fibrous catalyst); 2 – blank experiment 2 ($[H_2O_2]$ = 350 mg/L, no bubbled air, no fibrous catalyst); 3 – catalytic oxidation (bubbled air supply 5 L/min, fibrous catalyst, $[Fe^{3+}]$ on catalyst = 0.9 mmol/g); 4 – catalytic oxidation (fibrous catalyst, $[Fe^{3+}]$ on catalyst = 0.9 mmol/g, ($[H_2O_2]$ = 350 mg/L)

Effect of temperature on Sulfonl-NP catalytic degradation was investigated in temperature range 25-

40^0C. Activation energy of Sulfonol catalytic oxidation calculated using the experimental data is 32 kJ/mol.

4. Conclusions

The data presented above have shown that modification of PAN with aqueous solution of ethylenediamine and hydroxylamine introduces ion-exchange groups to the fibre. Formation of functional groups occurs mostly on the surface of the fibre. These newly formed groups can bind cations of multivalent metals (e.g. Fe^{3+}). According to SEM/EDX data, penetration of iron into the fibre is 5 μm. Thus, the modified and impregnated with ferric salt PAN fibre can be used as a catalyst for decomposition of organics. The external diffusion of the substrate can be overcome due to distribution of active sites on the surface of the fibre.

A slightly different modification of PAN produces a fibrous catalyst that can be effectively used for oxidation of phenol at room temperature using hydrogen peroxide as an oxidant.

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