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Preparation and characterization of ammoniated PAN nanofiber adsorbent

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Abstract: An ammoniated PAN nanofibers (PAN-NH_2) absorbent was prepared by grafting amino hyperbranched polymer (HBP-NH_2) onto polyacrylonitrile (PAN) nanofiber in presence of glutaraldehyde as a crosslinking agent. The structure and performance of PAN-NH_2 were characterized. The results indicated that HBP-NH_2 was successfully grafted onto PAN nanofibers surface by chemical crosslinking modification; PAN-NH_2 nanofiber provided the adsorption capacity up to 28.02 mg/g while used as an absorbent in the treatment of water containing Cu^{2+}; and the amino mass fraction of PAN-NH_2 fiber was 5.4%.

Key words: polyacrylonitrile fiber; nanofiber; absorbent; chemical crosslinking modification; heavy metal ion adsorption

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Nanofibers prepared by electrostatic spinning technique have become the focus of adsorption research in recent years[1-3] due to the advantage of large specific surface area and strong adsorption ability. Adsorption materials prepared by modified polyacrylonitrle (PAN) nanofibers have received much attention. Zhang Haitao et al. have prepared a kind of adsorption material by grafting chitosan onto PAN nanofiber membrane[2]. Khalid Saeed and Parvin Karimi Neghlani et al. have prepared ammoniated PAN nanofiber adsorption material by chemical modification[4-5]. The ammoniated PAN nanofibers had very good adsorption properties for Cu^{2+} and Pb^{2+}. However, the previous studies have been focused on grafting small molecular compounds to a nanofiber. It has not been reported that amino hyperbranched polymer (HBP-NH_2) can be grafted to PAN nanofibers for preparing of adsorbents for heavy metals up to now. Here we report an ammoniated PAN (PAN-NH_2) nanofiber adsorbent for heavy metals prepared by grafting HBP-NH_2 to PAN nanofibers.

1 Experiment

1.1 Raw material

PAN with the relative molecular mass of 8×10^4; All of the used chemical reagents, such as *N*,*N*-dimethylformamide (DMF), sodium hydroxide, hydrochloric acid, methyl acrylate, tetraethylenepentamine, methanol, glutaraldehyde (25% solution by mass fraction), salicylaldehyde, pyridine, sodium methoxide, phenolphthalein and copper(II) nitrate hydrate, were all analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

1.2 Electrospinning process

The spinning solution was prepared by dissolving 1 g PAN in 19 mL DMF aqueous and stirring for 12 h at room temperature in sealed state. The prepared spinning solution was pumped in a 20 mL plastic syringe of gauges with stainless steel needle. The electrolspinning voltage was maintained at 30 kV, the distance between the spinneret and collector was fixed as 16 cm, and the fitting speed was controlled at 0.015 mL/min.

1.3 Fiber pretreatment

A certain amount of PAN nanofibers were putted into NaOH solution with the mass fraction of 15% at the bath ratio of 1∶50, reacting for 60 min at 50 ℃. Then the reaction products were putted into HCl solution with the concentration of 1 mol/L, reacting at room temperature for 120 min[2]. The products were washed, dried and stoved for futher using.

1.4 Preparation of HBP-NH_2

HBP-NH_2 was synthesized by reacting tetraethylenepentamine (0.5 mol) with methyl acrylate (0.5 mol) according to the method described in literature [6].

1.5 Preparation of PAN-NH_2 nanofiber

A solution was prepared by adding 0.05 g PAN nanofibers into a 100 mL conical flask containing 5 mL distilled water, stirring and heating up to 70 ℃. A certain volume of glutaraldehyde was mixed with 2 mL distilled water, drippd into

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the solution containing PAN nanofibers, and then kept at 70 ℃ for 0.5 h. And a certain volume of 100 g/L HBP-NH_2 aqueous solution was added into the above solution, reacting for 2 h at 70 ℃. Hence, a tan PAN nanofiber adsorbent modified by HBP-NH_2 was obtained[2], which was filtered, washed and dried for adsorption. The mass fraction of amino was tested as 5.4% in the adsorbent by the salicylaldehyde method[7]. The reaction route is shown in Fig. 1.

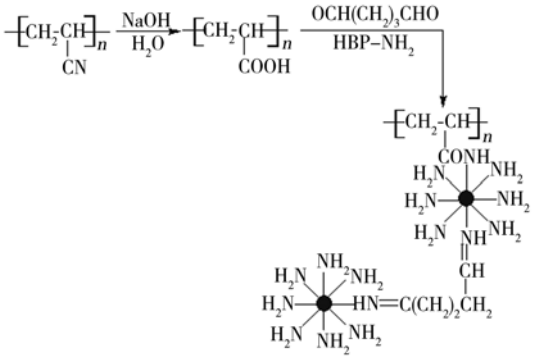

Fig. 1 Preparation of PAN-NH_2 nanofiber adsrobent

1.6 Analysis and test

The surface morphology of samples were observed by an S-4800 scanning electron microscope (SEM) (Hitachi, Japan). The FTIR spectra were recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Nicolet, USA) with a detector at 4 cm^{-1} resolution from 500 cm^{-1} to 4 000 cm^{-1} and 32 scans per sample. The heavy metal concentration of the initial and adsorbed solutions were measured by a Vista MPX inductively coupled plasma atomic emission spectrometer (ICP-OES) (Spectro Analytical Instruments GmbH, Germany).

2 Results and discussion

2.1 SEM analysis

It can be seen from Fig. 2 that PAN fibers had the even fineness in a clearly separated state. After modification by HBP-NH_2, PAN nanofibers became thicker, and the fiber surface was covered with a layer of crosslinking matter, which was the crosslinking product of HBP-NH_2 and glutaraldehyde. It was shown that HBP-NH_2 was linked onto PAN nanofibers surface via chemical grafting.

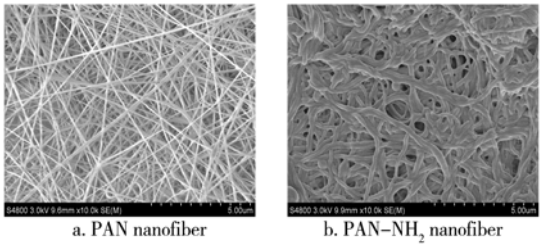

Fig. 2 SEM photographs of PAN and PAN-NH_2 nanofibers

2.2 FTIR spectrometry

As shown in Fig. 3, new characteristic peaks appeared in the infrared spectrum of PAN nanofiber modified by HBP-NH_2. The bending vibration peak of amino groups appeared at 1 635.41 cm^{-1} and 1 558.27 cm^{-1}, the stretching vibration peak of aldehyde group appeared at 2 931.39 cm^{-1} and 2 829.18 cm^{-1}[2,8-9]. The emergence of these new characteristic peaks showed that HBP-NH_2 had been grafted to the surface of PAN nanofibers via glutaraldehyde crosslinking. It also confirmed the phenomenon of the SEM figure appeared furtherly.

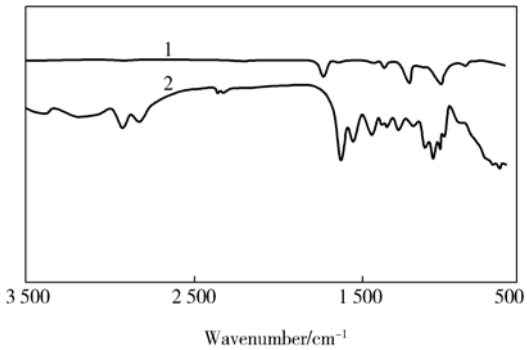

Fig. 3 FTIR spectra of PAN and PAN-NH_2 nanofibers
1—PAN nanofiber;2—PAN-NH_2 nanofiber

2.3 Heavy metal ions adsorption

0.1 g PAN nanofiber and 0.1 g PAN-NH_2 nanofiber were put into two 100 mL conical flasks separately and were mixed with 50 mL 100 μg/g Cu^{2+} solution, shaking for 4 h at 30 ℃ in water bath. The adsorption results were shown in Tab. 1.

As seen in Tab. 1, the adsorption capacity of PAN nanofibers for Cu^{2+} was 1.31 mg/g while the adsorption of PAN-NH_2 nanofibers for Cu^{2+} was up to 28.02 mg/g. PAN-NH_2 nanofiber had the adsorption capacity for Cu^{2+} greatly improved and showed excellent heavy metal adsorption ability due to the chelation between amino groups and Cu^{2+} metal ions[11]. An abundant of amino groups which could chelate with Cu^{2+} were introduced to PAN nanofibers after HBP-NH_2 grafting onto the fiber surface, so the adsorption of PAN-NH_2 nanofibers for Cu^{2+} had been greatly improved after modification by HBP-NH_2.

Tab. 1 Contrast of Cu^{2+} adsorption between PAN and PAN-NH_2 nanofibers

Samples	Adsorption capacity for Cu^{2+}/(mg · g^{-1})
PAN nanofiber	1.31
PAN-NH_2 nanofiber	28.02

3 Conclusions

a. A PAN-NH_2 nanofiber absorbent was prepared by the modification of PAN nanofibers using HBP-NH_2.

b. The experimental results showed that the amino mass fraction of PAN-NH_2 was up to 5.4% after modification and HBP-NH_2 was linked onto the surface of PAN nanofibers via chemical grafting.

c. The adsorption of PAN-NH_2 nanofibers for Cu^{2+} had been greatly improved after modification by HBP-NH_2, the adsorption capacity for Cu^{2+} reached 28.02 mg/g, and the PAN-NH_2 nanofiber was a good absorbent for Cu^{2+} heavy metal treatment in water.

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多氨基改性 PAN 纳米纤维吸附剂的制备与表征

臧传锋, 任　煜, 张广宇(南通大学纺织服装学院, 江苏 南通 226019)　**摘要:** 以聚丙烯腈(PAN)纳米纤维为基体, 利用多氨基超支化聚合物(HBP-NH_2)末端所具有的大量氨基官能团, 采用戊二醛作为交联剂, 将 HBP-NH_2 接枝到 PAN 纳米纤维上制备了多氨基改性 PAN 纳米纤维吸附剂(PAN-NH_2), 对 PAN- NH_2 的结构与性能进行了表征。结果表明: HBP-NH_2 通过化学交联成功接枝到 PAN 纳米纤维的表面; PAN-NH_2 用于含重金属离子 Cu^{2+} 的水体吸附, 对 Cu^{2+} 的吸附量可达 28.02 mg/g; PAN-NH_2 纤维的氨基质量分数高达 5.4%。**关键词:** 聚丙烯腈纤维　纳米纤维　吸附剂　化学交联改性　重金属离子　吸附性能