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Preparation and characterization of a new low-cost polyacrylonitrile adsorbent

Hayat Bouchoum1,2,5, Mehdi El Bouchti1, Amane Jada3,4, Mohamed Tahiri2, and Omar Cherkaoui1

1 Laboratory REMTEX, Higher school of textile and clothing industries, Casablanca, Morocco.
2 Hassan II University, faculty of science Ain Chok, Laboratory of geosciences, Casablanca, Morocco.
3 Univ Haute Alsace, CNRS, IS2M, UMR7361, F-68100 Mulhouse, France
4 Univ Strasbourg, Strasbourg, France
5 Author to whom any correspondence should be addressed

bouchoum.hayat@gmail.com

Abstract. Amidoximated polyacrylonitrile fibers (AO-PANF) was synthesized using hydroxylamine chelating agent to prepare an effective adsorbent for heavy metal and dyes removal. This study is the continuation of an earlier study and focuses on the characterization of the adsorbent. The thermal properties of adsorbent were evaluated using TGA and DSC analysis. The mechanical properties of the adsorbent were also been investigated. Characterization results reveal an improvement of thermal stabilities due to the modification process using hydroxylamine chelating agent. However, a reduction in mechanical properties was showed.

1. Introduction

Adsorption technology is considered to be the most effective and economical method to remove pollutants from aqueous solutions due to its high removal percentage, simple process and adsorbent recovery [1, 2]. The efficiency of adsorption process and economic sustainability depends mainly on the nature of the adsorbents used to remove pollutants from aqueous solutions [3, 4]. The surface modification is an important step to prepare an effective adsorbent for pollutants removal.

Polyacrylonitrile is the most polymeric material used for water purification. It is a commercial and low-cost polymer material with good mechanical, chemical and thermal stability as well as a good resistance to corrosion and solvents [1]. It has been used to produce variety of products such as activated carbon [5], nanofibers [1], composite materials [6], protective materials [7], heavy metals adsorbents [8], conductive materials [9] and others. Polyacrylonitrile fibers (PANF) is characterized by a large surface area and short diffusion distance [10], facilitating the adsorption of metals ions from aqueous solutions. It contain hydroxyl (OH) and amino groups (NH2) in their backbone making it a good adsorbent for water purification, heavy metals and dyes removal from aqueous solutions [11].
Chemical modification of polyacrylonitrile fibers (PANF) surface with hydroxylamine, diethylenetriamine [10], ethylenediamine, triethylenetetramine [8], carboxyl and imidazole [1] improve their properties and enhance the adsorption efficiency of the material. Among these chelating agents, hydroxylamine is promising, containing nitrogen and oxygen atoms, which have a strong affinity towards heavy metals ions. Nitrile groups containing on polyacrylonitrile surface can be easily transformed onto a variety of functional groups (carboxyl, amine, amidoxime, phosphoric, etc…).

In our previous study, we confirmed the capacity of the adsorbent to remove hexavalent chromium from aqueous solutions. In this study, we investigated the mechanical and thermal properties of the adsorbent before and after the modification process.

2. Materials and methods

2.1. Materials
Commercial polyacrylonitrile fibers (PANF) was cut, washed with distillated water and then dried in an oven. Hydroxylamine Hydrochloride, with a purity >99%, was purchased from Scharlab. NaOH and HCl were used to adjust the pH of the solution.

2.2 Surface modification
The surface modification of AO-PANF by one step reaction was done according to the procedure in our previous researches [12]. The modification consists of the conversion of the nitrile groups on PANF surface onto amidoximes groups, using Hydroxylamine Hydrochloride while respecting the cost of production. After the treatment, the adsorbents were separated from the solution by filtration, washed and dried for one day at 60°C. The modification of PANF using 0.15 M of hydroxylamine for 60 min at 70°C was found to produce a high conversion rate of nitrile groups of 33.7 % and acceptable mechanical properties. The FTIR spectroscopy, SEM analysis and calculating the conversion of nitrile groups were also studied in our previous work [12].

2.3 Samples analysis
2.3.1 Mechanical properties. The mechanical properties of the samples were investigated by measuring the elongation at break and breaking strength using an electronic tensile tester (LUDWIC mpk) according to NF EN ISO 2062. The samples were dried before the measurement for 1 H at 40°C to remove the water molecules.

2.3.2 Thermal analysis. Weight change with temperature was determined by thermogravimetric analysis (TGA) using Cahn Versa Therm analyzer under air atmosphere (25 ml.min⁻¹) from room temperature to 600°C with a heating rate of 10°C.min⁻¹. As a complementary to TGA analysis, differential scanning calorimetry (DSC) was performed to study the thermal behaviors of samples using Setaram DSC Evo 131 analyzer under nitrogen atmosphere 30 ml.min⁻¹ with 10 mg of samples in a temperature range of 40°C to 400°C at a heating rate of 10°C.min⁻¹.

3. Results and discussions

3.1. Thermogravimetric analysis
The weight loss of PANF, AO-PANF and AO-PANF-Cu (II) complexes during stabilization process was determined using thermogravimetric analysis (TGA-DTG) and is shown in (Figure 1). The dTg curves (Figure 1-b) demonstrate better the degradation steps of the samples.

Raw PANF show two degradation steps (Figure 1-a). The first degradation step with a small weight loss was observed between 50°C and 120°C due to the release of moisture [13], which was also observed for AO-PANF and AO-PANF- Cu (II) complexes. The onset degradation of PANF was
observed occurring from 290 to 430°C with the main weight loss of 32.46%. The degradation can be attributed to the release of nitrogenous gases from the cyclization, dehydrogenation or cross-linking reaction of nitrile groups containing on PANF surface [14]. Beyond 430°C, the thermal degradation of PANF backbone chains occurs [13]. The results is in accordance with previous studies [15].

Compared to PANF, the decomposition temperature of AO-PANF starts at a lower temperature of 197°C and continues up to 310°C with a weight loss of 9.81% due to the decomposition of grafted functional groups on AO-PANF surface [16]. The reduction is due to the presence of amidoximes group on AO-PANF surface indicating that it was beneficial for further cyclization.

The last degradation step occurs between 380°C and 470°C, the main weight loss of 9.14% was observed due to the thermal decomposition and carbonization process of AO-PANF. The residual weight at 600°C was 63% suggesting that AO-PANF is a suitable support for industrial wastewater treatment.

The residual weight of AO-PANF is 63% higher than PANF (59.9%) demonstrating the improvement of thermal stability of samples using hydroxylamine chelating agents.

After adsorption of copper, a significant change was observed on the adsorbent with a rapid thermal decomposition of 33.59% between 390°C and 520°C. The results evince that the AO-PANF-Cu (II) complexes metals adsorbed onto AO-PANF become less stable with a yield residual weight of 30%.

![Figure 1. TG (a) and dTg curves (b) of PANF, AO-PANF (C(NH₂OH) = 0.15 M) and AO-PANF-Cu (II) complexes (C (Cu II) = 15 mg L⁻¹) in air atmosphere.](image)

3.2. Differential scanning calorimetry (DSC)

The thermal properties of raw PANF and AO-PANF was achieved using a DSC analyzer from a single heating process and the results is shown in Figure 2. The highly exothermic peaks of PAN and AO-PANF, in nitrogen atmosphere, were observed at 316°C and 263°C, respectively. This reaction indicates the cyclization reactions of nitrile groups containing in PANF during the thermal process [17] and confirms the results obtained in thermogravimetric analysis section. This results is in agreement with the previous study [18]. The shift of exothermic peak for AO-PANF at lower temperatures indicated that the modification with hydroxylamine hydrochloride affects the cyclization mechanism of PANF in which the reaction starts easily by ionic mechanism. The amount of heat liberated during this process was different. The raw PANF compared to AO-PANF had a strong and sharp exothermic peak with an enthalpy of 50.442 J.g⁻¹, whereas AO-PANF demonstrated a broader peak with an enthalpy of 52.64 J.g⁻¹. The reduction of intensity of cyclization reaction for AO-PANF can reduce the structural defect formed in the final carbon material [19]. Additionally, AO-PANF showed an endothermic peak at 103°C which can be due to the removal of moisture generated by the addition of functional groups on PANF surface making it strongly hydrophilic [18]. In PANF, no endothermic peaks was observed suggesting that it is not melt at this heating rate [15].
3.3. Mechanical analysis

The mechanical properties were investigated in order to study the effect of the modification on the mechanical properties of the adsorbent. Previous works mentioned that the treatment with amidoximes groups tends to reduce the mechanical strength of original PANF [20, 21]. Table 1 regroups the mechanical parameters of PANF and AO-PANF. From Table 1, a comparison between raw PANF and AO-PANF showed a decrease in mechanical properties, making AO-PANF less resistive. These results were in accordance with the morphological structures observed previously by SEM analysis [12]. This can be due to the amidoximation process which generates a low crystallinity of AO-PANF [18].

Table 1: Mechanical parameters of PANF and AO-PANF (C(NH₂OH) = 0.15 M)

| Samples    | Tensile Strength (MPa) | Strain ε (%) | Tensile Modulus (MPa) |
|------------|------------------------|--------------|-----------------------|
| PANF       | 482                    | 26.31        | 29.47                 |
| AO-PANF    | 143.37                 | 21.54        | 13.68                 |

4. Conclusions

This study presented a synthesis procedure of an adsorbent compound of polyacrylonitrile fiber using hydroxylamine chelating agent. The thermal and mechanical properties of the adsorbent before and after modification process has also been investigated. The capacity of AO-PANF to remove heavy metals ions from aqueous solutions was confirmed in our previous studies. According to the results, in the thermal analysis, the comparison between raw PANF and AO-PANF showed an improvement of thermal stabilities due to the use of hydroxylamine chelating agents. However, AO-PANF showed a reduction on the mechanical strength. This can be due to the low crystallinity of AO-PANF.
References

[1] Ndayambaje G, et al., 2016 Adsorption of nickel (II) on polyacrylonitrile nanofiber modified with 2- (2′-pyridyl) imidazole. Chemical Engineering Journal 284: p. 1106-1116.

[2] Hassan A and R Bulánek 2019. Preparation and characterization of thiosemicarbazide functionalized graphene oxide as nanoadsorbent sheets for removal of lead cations. International Journal of Environmental Science and Technology, 16(10) p. 6207-6216.

[3] Weng C H, et al., 2007 Adsorption characteristics of copper (II) onto spent activated clay. Separation and Purification Technology 54(2) p. 187-197.

[4] Ghariani, B., et al., 2019 Porous heat-treated fungal biomass: preparation, characterization and application for removal of textile dyes from aqueous solutions. Journal of Porous Materials p. 1-14.

[5] Arbab S and A Zeinolebadi 2013 A procedure for precise determination of thermal stabilization reactions in carbon fiber precursors. Polymer degradation and stability, 98(12) p. 2537-2545.

[6] Yavuz M, et al. 2008 An economic removal of Cu2+ and Cr3+ on the new adsorbents: Pumice and polyacrylonitrile/pumice composite. Chemical Engineering Journal 137(3) p. 453-461.

[7] Kharaghani D, et al., 2018 Preparation and in-vitro assessment of hierarchal organized antibacterial breath mask based on polyacrylonitrile/silver (PAN/AgNPs) nanofiber. Nanomaterials, 8(7): p. 461.

[8] Soltanzadeh M, G Kiani and Khataee A 2014 Adsorptive capacity of polyacrylonitrile modified with triethylenetetramine for removal of copper and cadmium ions from aqueous solutions. Environmental Progress & Sustainable Energy 33(4) p. 1139-1147.

[9] Koutsonas S 2017 Electrical conductivity of degraded polyacrylonitrile powder by microwave irradiation for supercapacitor devices or other mobile applications. Materials Letters 193 p. 203-205.

[10] Abdouss M et al., 2012 Fabrication of chelating diethylenetriaminated pan micro and nano fibers for heavy metal removal. Chemical Industry and Chemical Engineering Quarterly 18(1) p. 27-34.

[11] Ibrahim A G, et al. 2019 Chitosan-g-maleic acid for effective removal of copper and nickel ions from their solutions. Int J Biol Macromol, 121 p. 1287-1294.

[12] Bouchoum H, et al. 2019 Synthesis of amidoximated polyacrylonitrile fibers and its use as adsorbent for Cr (VI) ions removal from aqueous solutions. Environmental Progress & Sustainable Energy.

[13] Cheng, Y., et al., 2019 Polyamine and amidoxime groups modified bifunctional polyacrylonitrile-based ion exchange fibers for highly efficient extraction of U (VI) from real uranium mine water. Chemical Engineering Journal.

[14] Chaúque E F, et al. 2016 Modification of electrospun polyacrylonitrile nanofibers with EDTA for the removal of Cd and Cr ions from water effluents. Applied Surface Science 369 p. 19-28.

[15] Mapazi O et al. 2018 High temperature thermochromic polydiacetylene supported on polyacrylonitrile nanofibers. Polymer 149 p. 106-116.

[16] Chen C et al., 2019 Preparation and Performance of Aminated Polyacrylonitrile Nanofibers for Highly Efficient Copper Ion Removal. Colloids and Surfaces A: Physicochemical and Engineering Aspects.

[17] Kim S S and Lee J 2014 Antibacterial activity of polyacrylonitrile–chitosan electrospun nanofibers. Carbohydr Polym, 102 p. 231-237.

[18] Han, Z., Y. Dong, and S. Dong, 2010 Comparative study on the mechanical and thermal properties of two different modified PAN fibers and their Fe complexes. Materials & Design, 31(6) p. 2784-2789.

[19] Korobeinyk A V, Whityby R L and Mikhalsky V S 2012 High temperature oxidative resistance of polyacrylonitrile-methylmethacrylate copolymer powder converting to a carbonized
monolith. European Polymer Journal 48(1) p. 97-104.

[20] Xu G., et al. 2018 Highly selective and efficient adsorption of Hg2+ by a recyclable aminophosphonic acid functionalized polyacrylonitrile fiber. Journal of Hazardous Materials 344 p. 679-688.

[21] Wu D, et al. 2018 Electrospun blend nanofiber membrane consisting of polyurethane, amidoxime polyacrylonitrile, and β-cyclodextrin as high-performance carrier/support for efficient and reusable immobilization of laccase. Chemical Engineering Journal 331 p. 517-526.