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# Synthesis of polyacrylamide-bound hydroquinone via a homolytic pathway: Application to the removal of heavy metals<sup>☆</sup>

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## ABSTRACT

Polyacrylamide (PAAm) was chemically modified with hydroquinone (HQ) via a homolytic route. A degree of modification of approximately 58% was obtained under optimal reaction conditions: time of 6 h, and [modifier]/[acrylamide] molar ratio of 5. PAAm and its modified form HQ-PAAm were characterized by UV-visible spectroscopy, FT-IR spectroscopy, <sup>13</sup>C NMR spectroscopy, DSC, TGA, XRD, and SEM. A relatively lower molecular weight of the corresponding hydroquinone-functionalized form was measured. The glass transition temperature of the modified polymeric material was lower than that of the pristine one: 78.82 °C for HQ-PAAm versus 161.19 °C for PAAm. A study of Cu(II) adsorption by the cross-linked PAAm and HQ-PAAm resins was conducted by varying the following parameters: pH, time, temperature, ionic strength, sorbent mass, and initial Cu(II) concentration. The adsorption capacity of Pb(II) and Cd(II) by the different resins and their corresponding extents of desorption were estimated. The optimal conditions for metal ion uptake by polyacrylamide and its modified resin were: pH = 5.4, time = 120 min, temperature = 45 °C. The sorption extent by the modified resin was in the order Pb(II) > Cu(II) > Cd(II). The desorption of the experimented metallic ions from the resins exceeded 97%. A new way of cross-linking PAAm and its modified form is described herein.

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## R É S U M É

Le polyacrylamide (PAAm) a été modifié chimiquement par l'hydroquinone (HQ) selon une voie homolytique. Un degré de modification d'approximativement 58 % a été obtenu dans les conditions de réaction optimales : temps de 6 h, rapport molaire [modifiant]/[acrylamide] de 5. Le PAAm et sa forme modifiée HQ-PAAm ont été caractérisés par spectroscopie UV-visible, spectroscopie FT-IR, spectroscopie <sup>13</sup>C RMN, calorimétrie différentielle à balayage (DSC), analyse thermogravimétrique (ATG), diffraction de rayons X (DXR) et microscopie électronique à balayage (MEB). La masse moléculaire moyenne du

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HQ-PAAm était relativement basse. La température de transition vitreuse du PAAm modifié était plus basse que celle du PAAm : 78,82 °C pour HQ-PAAm, contre 161,19 °C pour le PAAm. Une étude de l'adsorption du Cu(II) par les résines à base de PAAm et de HQ-PAAm réticulés a été menée en faisant varier les paramètres suivants : pH, temps, température, force ionique, masse du sorbant et concentration initiale en Cu(II). Les capacités d'adsorption de Pb(II) et Cd(II) par les résines et les taux de leur désorption ont été estimées. Le taux d'adsorption par la résine modifiée variait dans l'ordre Pb(II) > Cu(II) > Cd(II). La désorption des ions métalliques dépassait 97 %. Une nouvelle voie de réticulation de PAAm et sa forme modifiée est décrite.

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## 1. Introduction

Polyacrylamide (PAAm) stands as a versatile reactive polymer, largely due to its amide functionality. The amino group of the amide functionality facilitates the cross-linking of PAAm, and, interestingly, the resulting network has been efficient in the decontamination of soil and surfaces polluted by cesium and strontium following a nuclear accident [1]. Aminophenyl glycosides have been chemically attached to polyacrylamide to serve as affinity columns in cell filtration [2]. In its grafted form, PAAm was transformed into polyvinylamines as ion exchangers and flocculants by Hofmann degradation and Mannich reaction [3–5]. Sulfomethylated high-molecular-weight PAAm was obtained by reaction with formaldehyde and bisulfate [6]. The *N*-alkylation of the amide groups of polyacrylamide with *n*-alkyl bromide was conducted in DMSO and in the presence of potassium *tert*-butoxide [7]. PAAm-bound Schiff bases were employed as ligands for cobalt complexes, which are designed for the selective oxidation of olefins and alkyl halides [8]. PAAm hydrogels have been generated by hydrophobic modification via alkyl chains [9]. Polyacrylamide can be homolytically functionalized on its polyethylenic chain when a  $\gamma$ -irradiation source is applied. The latter technique was successful for grafting poly(4-vinylpyridine) onto PAAm [10]. Poly(*N*-2-aminoethylacrylamide) from the transamidation of PAAm with ethylenediamine was used as a chelating material for liquid chromatography [11]. However, polymers bearing polyhydroxylated benzene moieties, namely dihydroxybenzenes and their corresponding benzoquinones, display distinct properties and have been utilized in various applications [12–14]. Producing poly(vinyl-polyhydroxybenzene)s, such as poly(vinylhydroquinone), is unfortunately not a straightforward task, as the phenol functionality is sensitive to the polymerization conditions; moreover, it is typical to protect this functionality in the vinyl monomer prior to polymerization and to deprotect it afterwards.

Thus, incorporating polyhydroxylated benzene onto a premade polymeric matrix has been considered as a good alternative. Yoshida et al. [15] prepared a polymeric material from a ligninocatechol by means of a laccase-catalyzed polymerization, an environmentally friendly procedure. McGrath and co-workers [16] showed the potential applications of a partially disulfonated hydroquinone (HQ)-based poly(arylene ether sulfone) random copolymer as a proton exchange membrane. Gurnule et al.

[17] evaluated 2,4-dihydroxybenzophenone-oxamide-formaldehyde terpolymers as ion-exchanging resins for Cu(II), Hg(II), Cd(II), Co(II), Zn(II), Ni(II), Pb(II), and Fe(III).

To continue our ongoing work on the functionalization of polyacrylics [18–21], we report herein the results of the chemical modification of polyacrylamide (PAAm) with a hydroquinone (HQ) entity by applying the conditions of Minisci [22] and the metallic adsorption properties of PAAm and the modified polymer.

## 2. Experimental

### 2.1. Methods and materials

Polyacrylamide was prepared according to a previously reported procedure [21]. Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was recrystallized from water. 1,4-Benzoquinone (BQ), silver nitrate (AgNO<sub>3</sub>), copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, lead nitrate Pb(NO<sub>3</sub>)<sub>2</sub>, and cadmium nitrate Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were used as purchased. Chemicals were purchased from one of the following suppliers: Aldrich, Fluka AG, Prolabo, and Merck.

UV–Vis spectra were recorded using a JASCO UV–Vis spectrophotometer; bi-distilled water was employed as the solvent. Infrared spectra were taken with a JASCO 4200 FT–IR instrument. Polymer samples used for infrared analysis were in the form of cast films. <sup>13</sup>C NMR spectra were recorded using a Bruker 400 MHz spectrometer at the Laboratoire Méthodologie RMN (FR CNRS 2843, UMR UHP–CNRS CRM2 7036), Université Henri-Poincaré (UHP) (France) with D<sub>2</sub>O as the solvent. XRD analysis of thin films were recorded using a Bruker D8 X-ray diffractometer (radiation Cu K $\alpha$ ,  $\lambda$  = 0.154 nm, 40 kV, 100 mA), at a  $2\theta$  grazing angle from 5° to 90° at a scan rate of 0.02°/s. SEM images of the polymers were taken using a JOEL JSM-6700F scanning electron microscope operating at an accelerating voltage of 3 kV. DSC thermograms were recorded on a Netzsch DSC 204 F1 fitted with an electronic module for nitrogen liquid cooling. Temperature and enthalpy calibrations were set with indium, and an empty aluminum pan was taken as a reference. Samples of weights in the 5–10-mg range were heated up to 120 °C at a heating rate of 20 °C/min under nitrogen flow, followed by quenching to 25 °C using liquid nitrogen. The DSC curves were recorded during the second heating cycle at a heating rate of 5 °C/min up to 250 °C, and the values of  $T_g$  were then determined according to the tangent method. TGA curves were recorded on a TGA Q500 thermogravimetric analyzer

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