



# Cationic hemicellulose-based hydrogels for arsenic and chromium removal from aqueous solutions



Daniel Dax<sup>a,\*</sup>, María Soledad Chávez<sup>b,c</sup>, Chunlin Xu<sup>a,d</sup>, Stefan Willför<sup>a</sup>,  
Regis Teixeira Mendonça<sup>b,e</sup>, Julio Sánchez<sup>c,\*\*</sup>

<sup>a</sup> Process Chemistry Centre, c/o Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Porthansgatan 3, 20500 Åbo/Turku, Finland

<sup>b</sup> Centro de Biotecnología, Universidad de Concepción, Casilla 160-C, Concepción, Chile

<sup>c</sup> Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

<sup>d</sup> Wallenberg Wood Science Center, KTH, The Royal Institute of Technology, 10044 Stockholm, Sweden

<sup>e</sup> Facultad de Ciencias Forestales, Universidad de Concepción, Casilla 160-C, Concepción, Chile

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## ABSTRACT

In this work the synthesis of hemicellulose-based hydrogels and their application for the removal of arsenic and chromium ions is described. In a first step *O*-acetyl galactoglucomannan (GGM) was subjected to a transesterification applying glycidyl methacrylate (GMA) for the synthesis of novel GGM macromonomers. Two distinguished and purified GGM fractions with molar mass of 7.1 and 28 kDa were used as starting materials. The resulting GGM macromonomers (GGM-MA) contained well-defined amounts of methacrylate groups as determined by <sup>1</sup>H NMR spectroscopy. Selected GGM-MA derivatives were consecutively applied as a crosslinker in the synthesis of tailored hydrogels using [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MeDMA) as monomer. The swelling rate of the hydrogels was determined and the coherence between the swelling rate and the hydrogel composition was examined. The morphology of the GGM-based hydrogels was analysed by SEM and the hydrogels revealed a high surface area and were assessed in respect to their ability to remove arsenate and chromate ions from aqueous solutions. The presented bio-based hydrogels are of high interest especially for the mining industries as a sustainable material for the treatment of their highly contaminated wastewaters.

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## 1. Introduction

The rapid growth of the world population and the increasing living standard in developing countries leads to a constant augmentation of the need for construction materials, electronic components, and energy resources. Therefore, worldwide oil and coal, resp. ore deposits are exploited. Beside various other problems, one threatening side effect of the exploitation of ores is that the local environment is often highly contaminated with toxic heavy metals and metalloids such as mercury (Hg), chromium (Cr), arsenic (As), lead (Pb), cadmium (Cd), and zinc (Zn). Ions of these metallic species are found in the industrial wastewaters and they can be accumulated in the environment and tissues causing various diseases and disorders in living organisms. Because heavy metal ions show toxic effects even at very low dosages,

an effective wastewater treatment is essential to avoid unnecessary exposure of the population in the surroundings of ore mines. Several methods for the removal of metal ions are known, such as the adsorption of metal ions on activated carbon (Faulconer, von Reitzenstein, & Mazyck, 2012), application of chelating or ion exchange resins (Zainol & Nicol, 2009), zeolites (Ali, Thabet, El-Nasser, Hassan, & Salama, 2012), as well as the use of synthetic polymers (Rivas, Pereira, Gallegos, & Geckeler, 2002; Rivas, Pereira, Palencia, & Sánchez, 2011) and chemical precipitations (Feng, Aldrich, & Tan, 2000). Nevertheless, these techniques have several inherent disadvantages such as high costs, formation of toxic sludge, and other waste products, which have to be disposed (Peng, Ren, et al. 2012; Peng, Zhong, et al. 2012). Extensive efforts are thus made in order to produce more efficient, environmentally friendly (e.g. biobased), and reusable materials for heavy metal removal from wastewaters. In the last decade, different plant materials such as lignin (Guo, Zhang, & Shan, 2008), cellulose (Akama & Ueda, 2013), chitin/chitosan (Ayoub, Venditti, Pawlak, Salam, & Hubbe, 2013; Zheng, Wang, Zhu, & Wang, 2013), hemicelluloses (Peng, Ren, et al. 2012; Peng, Zhong, et al.

\* Corresponding author. Tel.: +358 2215 4886; fax: +358 2215 4868.

\*\* Corresponding author. Tel.: +56 041 2207028; fax: +56 041 2245974.

E-mail addresses: [ddax@abo.fi](mailto:ddax@abo.fi) (D. Dax), [juliosanchez@udec.cl](mailto:juliosanchez@udec.cl) (J. Sánchez).

2012), agriculture wastes (Ahluwalia & Goyal, 2005; Wan Ngah & Hanafiah, 2008), starch (Apopei, Dinu, Trochimczuk, & Dragan, 2012) and bark (Netzahuatl-Muñoz, Guillén-Jiménez, Chávez-Gómez, Villegas-Garrido, & Cristiani-Urbina, 2012; Palma, Freer, & Baeza, 2003) were tested in respect to their ability to absorb metal ions. From this list especially cellulose and hemicelluloses reveal a high potential due to their high abundance, as well as the already existing refining factories, e.g. pulp mills. Furthermore, the use of cellulose and hemicelluloses does not raise ethical issues because they cannot be used as food, what makes them favourable compared to starch.

One promising water-soluble hemicellulose is *O*-acetyl galactoglucomannan (GGM), which can be extracted from softwood by pressurized hot-water extraction (PHWE) (Al Manasrah, Kallioinen, Ilvesniemi, & Manttari, 2012) or recovered from the wastewaters of a thermomechanical pulping process by ultrafiltration (Lundqvist et al., 2003; Persson, Nordin, Zacchi, & Jónsson, 2007; Willför et al., 2003; Xu, Willför, Holmlund, & Holmbom, 2009). The circumstance that GGM is a side product of the pulping industry and hence available in large amounts, reveals the outstanding potential of GGM as a renewable raw material for novel functional products. GGM consists of a linear backbone of randomly distributed (1→4)-linked β-D-mannopyranosyl (Manp) and (1→4)-linked β-D-glucopyranosyl (Glc) units, with α-D-galactopyranosyl (Galp) units as single side units (Hannuksela & Hervé du Penhoat, 2004). GGM is partially acetylated and the *O*-acetyl groups are located randomly at C2 and C3 position of the mannose units in the main chain (Willför et al., 2003). In order to make GGM suitable for ion removal applications, water-soluble GGM derivatives bearing different, either charged or neutral, groups might be synthesized. The most convenient way to modify GGM is the substitution of the hydroxyl groups (Dax, Eklund, et al., 2013; Dax, Xu, et al., 2013; Voepel, Edlund, Albertsson, & Percec, 2011), but charged polymers can also be attached to the reducing end of GGM (Dax, Eklund, et al., 2013; Dax, Xu, et al., 2013). These GGM derivatives would be water-soluble and could be applied for metal removal in a similar way as water-soluble synthetic polymers. However, the complex setup needed when using water-soluble polymers makes it preferable to develop water-resistant products, such as hydrogels based on bio-renewable materials. These materials could be removed from the aqueous solution either by filtration or centrifugation, which makes the use of, e.g. expensive special membranes superfluous.

In this work, an effective way for the synthesis of novel, tailor-made GGM-based hydrogels with tuneable swelling rates is described. Two purified and well-characterized GGM fractions were in a first reaction step derivatized in a transesterification reaction with glycidyl methacrylate and analysed by <sup>1</sup>H and <sup>13</sup>C NMR. Subsequently, the GGM macromonomers were applied as bio-based crosslinkers in the production of several hydrogels using a methacrylic monomer bearing a quaternary ammonium group. The GGM-based hydrogels were tested with respect to their potential as a bioadsorbent by removing toxic As and Cr ions from aqueous solutions.

## 2. Experimental

### 2.1. Materials

Glycidyl methacrylate (GMA) 97% (Aldrich), ammonium persulfate 98% (Aldrich), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MeDMA) 80 wt.% in H<sub>2</sub>O (Aldrich), dimethyl sulfoxide (DMSO) (Merck), dimethylformamide (DMF) (Aldrich), acetone (J.T. Baker), 4-(dimethylamino)pyridine (DMAP) 98% (Aldrich), ethanol (EtOH) (Merck), Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (Merck), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Merck), NaOH (Merck), HNO<sub>3</sub> (Merck). DMSO and DMF

**Table 1**

Reaction conditions for the transesterification of GMA with GGM.

Crosslinker	T (°C)	GMA/X <sup>a</sup>	DMAP <sup>b</sup>	Solvent	MA per GGM chain <sup>c</sup>	DS <sub>MA</sub>
GGM5-MA0.04	50	5:7	5	DMF	0.97	0.03
GGM5-MA0.25	50	5:7	10	DMF	6.89	0.25
GGM5-MA0.32	50	5:7	20	DMF	8.87	0.32
GGM5-MA0.03	50	5:7	10	DMSO	0.87	0.03
GGM5-MA0.14	50	5:7	20	DMSO	3.78	0.14
GGM5-MA0.33	50	10:7	20	DMSO	9.23	0.33
GGM22-MA0.41	50	5:7	20	DMF	50.78	0.41
GGM22-MA0.32	50	5:7	20	DMSO	39.7	0.32
GGM22-MA0.20	50	2.5:7	20	DMSO	24.7	0.20

<sup>a</sup> Molar ratio of GMA to anhydrous sugar units of GGM.

<sup>b</sup> wt.% in respect to GGM.

<sup>c</sup> Average amount of MA groups present in each GGM chain.

were distilled to remove water. All the other materials were commercially available and were of reagent grade or better and were used without further purification.

Pressurized hot-water extracted *O*-acetyl galactoglucomannan (GGM) from Norway spruce (*Picea abies*) was provided by The Finnish Forest Research Institute Metla. The extraction conditions were studied and optimized in a previous study (Kilpeläinen, Kitunen, Pranovich, Ilvesmiemi, & Willför, 2013) and GGM was obtained as a solution with a concentration of 30 wt.%. The extract was further purified in order to remove impurities and to narrow down the molar mass distribution (low polydispersity (PDI)). Therefore, the concentrated GGM solution (330 mL) was diluted with water (670 mL) and then precipitated in 9 L of ethanol at room temperature. The colourless precipitate was filtrated off and consecutively washed with ethanol, acetone, and methyl *tert*-butyl ether and finally the solid GGM was freeze-dried. The purified GGM fraction was obtained with a weight average molar mass (*M<sub>w</sub>*) 7.1 kDa (polydispersity ~1.5). The second GGM fraction was prepared from the process water of spruce thermomechanical pulping (TMP) prior to any chemical treatments (Willför et al., 2003). In short, the process water was purified from colloidal wood resin, and aromatic residues using a cationic coagulant (Raifix 120, Raisio Chemicals Oy, Finland) and XAD-7 resin (Amberlite, Rohm and Haas, UK). The solution was concentrated under reduced pressure before GGM collected by precipitation in ethanol. The GGM was air-dried and its *M<sub>w</sub>* was 28 kDa (polydispersity ~1.3), as determined by HPSEC-RI/MALLS. In the following text the GGM fractions are referred as GGM5 (*M<sub>n</sub>* = 4.7 kDa) and GGM22 (*M<sub>n</sub>* = 21.5 kDa). The sugar unit ratio of GGM was determined by acid methanolysis and gas chromatography and was around 5–4:1:0.5–1.1(Man:Glc:Gal) (Willför, Sundberg, Tenkanen, & Holmbom, 2008) and the degree of acetylation (DS<sub>Ac</sub>) ~0.20.

### 2.2. Synthesis of GGM-MA macromonomers

The reaction conditions for the insertion of the methacrylate groups into the GGM chain were adjusted outgoing from a previous study (Peng, Ren, et al. 2012; Peng, Zhong, et al. 2012) by changing the temperature, the catalyst amounts, and the solvent. The parameters of the performed reactions are listed in Table 1. The exact procedure is exemplarily described for the product GGM5-MA0.03 (here 0.03 denotes the degree of substitution of GGM5). GGM5 (100 mg, 0.6 mmol of anhydrous sugar units, 1 equiv.) was dissolved in 3 mL of dry DMF at 50 °C. Consecutively DMAP (5 mg, 0.041 mmol, 5 wt.% in respect to GGM) and GMA (62 mg, 0.43 mmol, 0.7 equiv.) were added and the mixture was stirred under nitrogen atmosphere at 50 °C for 16 h. The reaction mixture was then transferred into a dialyses tube (cut-off of 2 kDa) and dialyzed against distilled water for 3 days with daily water

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