# Study of starch-graft-itaconic acid hydrogels in the batch adsorption of trivalent chromium Cr(III) and hexavalent chromium Cr(VI)

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February 2023

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

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List of tables	iii
List of figures	iv
Abstract	v
Résumé	vi
Acknowledgments	vii
Contribution of authors	viii
1. Introduction	1
1.1 General introduction	1
1.2 Study objectives	5
1.2.1. General objective	5
1.2.2. Specific objectives	5
1.3 Hypothesis	5
1.4 Thesis outline	5
2. The oxidation states of heavy metals and their adsorption behavior onto biobased hy	drogels
– A review	6
2.1 Abstract	6
2.2 Introduction	6
2.3 Biobased hydrogels for the adsorption of heavy metals	
2.4 Factors influencing the adsorption of heavy metals onto biobased hydrogels	9
2.5 Conclusions	
3. Connecting statement	19
4. Selective adsorption of Cr(III) over Cr(VI) by starch-graft-itaconic acid hydrogels	20
4.1 Abstract	20
4.2 Introduction	20
4.3 Materials and methods	
4.3.1. Materials	
4.3.2. Synthesis of starch-graft-itaconic acid hydrogels	
4.3.3. Point of zero charge of starch-graft-itaconic acid hydrogels	

## Table of contents

4.3.4. Effect of the pH on the water retention capacity of starch-graft-itaconic acid
hydrogels
4.3.5. Batch adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels 26
4.3.5.1. Effect of the Cr solution pH on the adsorption of Cr(III) and Cr(VI) by starch-
graft-itaconic acid hydrogels
4.3.5.2. Effect of the Cr solution volume on the adsorption of Cr(III) and Cr(VI) by
starch-graft-itaconic acid hydrogels
4.3.5.3. Binary component adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic
acid hydrogels
4.3.6. Analysis of the concentrations of Cr(III) and Cr(VI) in aqueous solution
4.4 Results and discussion
4.4.1. Point of zero charge of starch-graft-itaconic acid hydrogels
4.4.2. Effect of pH on the water retention capacity of starch-graft-itaconic acid hydrogels
4.4.3. Single-component adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid
hydrogels
4.4.4. Effect of Cr solution volume on the single-component adsorption of Cr(III) and
Cr(VI) by starch-graft-itaconic acid hydrogels
4.4.5. Binary adsorption of Cr(III) and Cr(VI)
4.5 Conclusions
5. General discussion and general conclusions
6. References

## List of tables

Table 2.1. Some heavy metals, their thermodynamically stable oxidation states, and their
maximum acceptable concentration in drinking water [50], [51]7
Table 2.2. Efficiency and estimated cost of the most common heavy metal water treatment
processes
<b>Table 2.3.</b> Biobased hydrogels for the adsorption of Cu(II). 10
<b>Table 2.4.</b> Functional groups of various biobased hydrogels for the adsorption of Cr(III).   11
Table 2.5. Adsorption capacity and reported adsorption mechanism of Cr(VI) onto various
biobased hydrogels
Table 2.6. Electronegativity and effective ionic radii (according to the coordination number) for
some metals
Table 2.7. Adsorption isotherm and kinetics models in the adsorption of heavy metals onto
biobased hydrogels
<b>Table 4.1.</b> Effect of pH on the adsorption of Cr(III) by starch-graft-itaconic acid hydrogels 32
<b>Table 4.2.</b> Effect of pH on the adsorption of Cr(VI) by starch-graft-itaconic acid hydrogels 32
Table 4.3. Adsorption capacity of starch-graft-itaconic acid hydrogels in comparison to other
adsorbents in the literature for Cr(III) adsorption
Table 4.4. Effect of chromium solution volume on the binary adsorption of Cr(III) and Cr(VI) by
starch-graft-itaconic acid hydrogels

# List of figures

Figure 1.1. General illustration of the water absorption by hydrogels. Adapted from Bhatnagar et
al. (2016) [33]
Figure 1.2. Illustration of some adsorption mechanisms of heavy metals by hydrogels. Reprinted
with permission from Badsha et al. (2021) [37] (Copyright Elsevier 2021)
Figure 4.1. Schematic illustration of starch-graft-itaconic acid hydrogel synthesis
Figure 4.2. Point of zero charge of starch-graft-itaconic acid hydrogels. Error bars with 95 %
confidence level from three replicates
Figure 4.3. Chemical structure of starch-graft-itaconic acid hydrogels. Adapted from Duquette et
al. (2020) [84]
Figure 4.4. Effect of pH of distilled water on the water retention capacity by starch-graft-itaconic
acid hydrogels. Error bars with 95 % confidence level from three replicates
Figure 4.5. Effect of pH on the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid
hydrogels. Error bars with 95 % confidence level from three replicates. *At pH 10, some
precipitation of Cr(III) occurred; therefore, the results are partly due to adsorption
Figure 4.6. Pourbaix diagram of Cr-H <sub>2</sub> O at 25 °C. Concentration of total $Cr = 10^{-6}$ M. The area
limited by the dotted lines represents the stability of water. Adapted from Markiewicz et al. (2015);
Liu et al. (2016); Zhang and Tian (2020) [94,180,181]
Figure 4.7. Effect of volume on the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid
hydrogels. Error bars with 95 % confidence level from three replicates. The pH of the chromium
solutions was not adjusted; the pH of Cr(III) was 3.1 and the pH of Cr(VI) was 4.5
Figure 4.8. Effect of chromium solution volume on the binary adsorption of Cr(III) and Cr(VI) by
starch-graft-itaconic acid hydrogels. The remaining volume fraction corresponds to Cr(VI). The
pH of the solution was not adjusted, and the pH of the binary mix was approximately 3.5. Error
bars with 95 % confidence level from three replicates

#### Abstract

Chromium-polluted water is a prevalent problem that threatens the environment and human health. Aqueous chromium is primarily in two oxidation states (i.e., Cr(III) and Cr(VI)), each with unique physicochemical properties and health implications. The long-term exposure causes gastrointestinal pain, vomiting, and damages to vital organs. Biobased superabsorbent hydrogels are hydrophilic crosslinked polymer networks which are promising materials for the adsorption of aqueous chromium. The objectives of this thesis were to review the literature on the application of biobased hydrogels for the adsorption of heavy metals, and to evaluate the effects of volume and pH on the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels. Starch-graftitaconic acid hydrogels were synthesized and tested in batch experiments at room temperature for 24 h with constant mixing. It was found that the hydrogels could selectively remove Cr(III) over Cr(VI), which was highly dependent on the pH of the solution, with a maximum adsorption at pH 8.0. The affinity of starch-graft-itaconic acid hydrogels for Cr(III) could be due to the electrostatic attraction between the positively ionic states of Cr(III) ions and the negatively charged surface of the hydrogels. This predominantly negative surface charge of the hydrogels might be attributed to the ionic state of their surface functional groups. Moreover, due to the carboxyl functional groups of the hydrogels, ion exchange and surface complexation may have also contributed to the higher adsorption of Cr(III) over Cr(VI). The findings of this work suggest the potential application of starch-graft-itaconic acid hydrogels in the selective adsorption of Cr(III) and provide further insight into the application of biobased hydrogels in the removal of heavy metals from contaminated water.

#### Résumé

L'eau polluée par le chrome est un problème répandu qui menace l'environnement et la santé humaine. Le chrome aqueux se trouve principalement dans deux états d'oxydation (c.-à-d. Cr(III) et Cr(VI)), chacun avec des propriétés physico-chimiques uniques et des implications pour la santé. L'exposition à long terme provoque des douleurs gastro-intestinales, des vomissements et des dommages aux organes vitaux. Les hydrogels super absorbants d'origine biologique sont des réseaux de polymères réticulés hydrophiles qui sont des matériaux prometteurs pour l'adsorption du chrome aqueux. Les objectifs de cette thèse étaient de passer en revue la littérature sur l'application des hydrogels d'origine biologique pour l'adsorption des métaux lourds, et d'évaluer les effets du volume et du pH sur l'adsorption de Cr(III) et Cr(VI) par des hydrogels formulés avec de l'amidon et de l'acide itaconique. Ces hydrogels ont été synthétisés et testés dans des expériences de type batch à température ambiante pendant 24 h. Il a été constaté que les hydrogels pouvaient éliminer sélectivement le Cr(III) qui dépendait fortement du pH de la solution, avec une adsorption maximale à pH 8,0. L'affinité des hydrogels pour Cr(III) est probablement due à l'attraction électrostatique entre l'état ionique positif des ions de Cr(III) et la surface négativement chargée des hydrogels. Cette charge de surface principalement négative des hydrogels pourrait être attribuée à l'état ionique de leurs groupes fonctionnels de surface. De plus, en raison des groupes fonctionnels carboxyle des hydrogels, l'échange d'ions et la complexation de surface peuvent également avoir contribué à l'adsorption plus élevée de Cr(III) sur Cr(VI). Les résultats de ces travaux suggèrent l'application potentielle d'hydrogels dans l'adsorption sélective du Cr(III) et fournissent un aperçu supplémentaire de l'application des hydrogels biosourcés dans l'élimination des métaux lourds de l'eau contaminée.

#### Acknowledgments

First and foremost, I would like to thank my supervisors, Dr. Marie-Josée Dumont and Dr. Jason Robert Tavares, for their encouragement, invaluable advice, and feedback.

I am thankful for the scholarship granted by the National Council for Science and Technology of Mexico (CONACYT), the graduate excellence award by McGill University, and the financial aid from my supervisors, provided by the Fonds de Recherche du Québec – Nature et technologies (FRQNT) and the Centre de Recherche sur les Systèmes Polymères et Composites à Haute Performance (CREPEC).

I would also like to express my gratitude to Mr. Ranjan Roy and Mr. Andrew Golsztajn for their help in the laboratory and throughout the experimental work.

To my laboratory colleagues, Ann Pille, Sofia Lecona, Nicole Bélanger, Amin Leamon, Surabhi Pandey, Fabiola Alcalde, and Derek Troiano, thank you for your friendship. I would like to thank Ann Pille in particular for assisting with the synthesis of hydrogels and her support during the first stages of my degree. I would also like to thank Wendell Raphael and David Brassard of Polytechnique Montréal for their invaluable help with some final experiments.

Sincere appreciation goes out to my friends Ivan Martinez, Diana Toscano, Melissa Almanza, Juan Castillo, Karen Morales, Rodrigo Quirino, Jonathan O'Connor, and Mathieu Beaupré.

Finally, I would like to express my heartfelt gratefulness to my parents and siblings for their unconditional support.

## **Contribution of authors**

Alexis Solis Ceballos, the MSc. candidate, conducted the experiments, analyzed the experimental data, drafted the manuscript, and prepared this thesis. Dr. Marie-Josée Dumont, supervisor of the candidate, Full Professor in the Department of Chemical Engineering at Université Laval and Adjunct Professor in the Department of Bioresource Engineering at McGill University, and Dr. Jason Robert Tavares, co-supervisor of the candidate, Full Professor in the Department of Chemical Engineering at Polytechnique Montréal, contributed to all aspects of this work, including their research expertise in the experimental design, manuscript review and editing, and funding. Mr. Ranjan Roy and Mr. Andrew Golsztajn, Analytical Laboratory technicians in the Department of Chemical Engineering at McGill University, helped with the protocol to determine the concentration of aqueous chromium using inductively coupled plasma – optical emission spectroscopy, and provided their expertise in the experimental work and analysis of the data.

#### 1. Introduction

#### 1.1 General introduction

Although heavy metals may be found in food, soil, and air, drinking water is probably the most prevalent source of heavy metal exposure [1]. A substantial source of heavy metals (e.g., lead, arsenic, chromium) that leach into aquifers and risk the safety of drinking water are industrial effluents (e.g., steel leaching, tannery industry, chrome plating industry) [2,3]. Polluted drinking water with metals affects over half of the world's population, and long-term exposure causes serious health issues such as muscular dystrophy and Parkinson's disease [4,5]. Metals such as chromium (Cr) is odorless and tasteless with average concentrations in Canadian drinking water between 0.0002 ppm and 0.002 ppm [6]. Even at such low concentrations, long-term exposure could cause cancers, internal bleeding, and damages to vital organs [7,8]. Furthermore, the physicochemical properties and noxiousness of Cr may differ significantly among their numerous thermodynamically stable oxidation states. Cr is commonly found in water as Cr(III) and Cr(VI), with Cr(VI) being substantially more poisonous than Cr(III) [9,10]. However, the excessive buildup of Cr(III) may also be detrimental for the environment, and under natural conditions, Cr(III) may oxidize to Cr(VI) [3].

Traditional methods for the treatment of chromium-polluted water, such as membrane filtration [11], ion exchange [12], and electrodialysis [13], require a considerable amount of energy, create secondary contaminants (e.g., sediments, chemicals), or are costly [14,15]. In contrast, adsorption is suitable for diluted metal solutions, is simple to implement, and requires low energy input compared to other approaches [16]. Heavy metal removal by adsorption can be up to 20 % more efficient, and \$250 US more economical per million liters of treated water than electrodialysis, for example [15]. Among common heavy metal adsorbent materials (e.g., polymers, zeolites, clay minerals, nanoparticles, activated carbon), activated carbon is one the most widely researched adsorbents mainly due to their physical properties such as regular structure, large surface area, and porosity [17]. However, commercially available activated carbon is usually expensive and not selective for heavy metal adsorption [18]. Therefore, researchers have studied more economically appealing adsorbents produced from natural wastes such as agricultural [19,20], animal [21], and industrial wastes [22]. These wastes were converted to activated carbons [23], powders [24], and polymers [25] to enhance their physicochemical properties and heavy metal adsorption capacity.

Polymers, for example, have shown outstanding properties such as ion exchange capability, strong affinity for heavy metals, and frequently simple production. For example, polyaniline- and polypyrrole-based polymers are conducting organic polymers characterized for their electrochemical and mechanical properties [26]. Polymer-based nanocomposites (i.e., multiphase materials with ceramics, metals, clays, or polymers) are also some new potential heavy metal adsorbents due to their stability, adjustable characteristics, and large surface area [27]. Another kind of polymers for the adsorption of heavy metals include ion-imprinted polymers, such as graphene oxide-mesoporous silica, which have a large surface area, fast kinetics, and high selectivity for Cr(VI) [28]. However, some drawbacks of these polymers is their complex synthesis process and slow mass transfer [29–31].

On the contrary, hydrogels are notable for their surface qualities, such as porous and hydrophilic structure formed by three-dimensional polymer networks. They are characterized by their exceptional ability to absorb and hold significant amounts of water [32]. Figure 1.1 shows the basic structure of hydrogels and their water absorption mechanism, which is due to the hydrophilic acid groups bound to the hydrogel main polymer chain [33]. Water enters the hydrogel structure through osmosis, causing hydrogen atoms to react and become part of aqueous solution as positive ions [33]. This results in a negatively charged surface polymer chain, which repels each other and causes the polymer chain to expand, while water molecules are attracted to the structure through hydrogen bonding [33].



Figure 1.1. General illustration of the water absorption by hydrogels. Adapted from Bhatnagar et al. (2016) [33].

Moreover, the properties of these polymers are often enhanced by the addition of several functional groups (e.g., amine, amide, quaternary ammonium, hydroxyl, carboxyl) that provide hydrogels the ability to adsorb and retain many pollutants present in water within their structure through electrostatic interactions, ion exchange, and surface complexation, for example (Figure 1.2) [34–37]. A significant advantage of these materials is that, in contrast to most adsorbents, which adsorb pollutants on the surface, hydrogels may adsorb heavy metals over a wider surface area due to their three-dimensional networks (i.e., more sites per unit volume), and the crosslinked network chains provide their resistance to dissolving in the aqueous solution [33].



Figure 1.2. Illustration of some adsorption mechanisms of heavy metals by hydrogels. Reprinted with permission from Badsha et al. (2021) [37] (Copyright Elsevier 2021).

Hydrogels comprised of natural sources such as starch, chitosan, and alginate, known as biobased hydrogels, are low-cost materials that have shown outstanding capacity for heavy metal removal from polluted water [17,38]. Starch is the most prevalent storage polymers found in many plants, whose physical properties such as size and shape vary depending on its provenance (e.g., corn, rice, wheat, potato, cassava) [39,40]. It is a biodegradable and renewable carbohydrate composed of two primary polysaccharides (amylose and amylopectin) with a high concentration of hydroxyl groups, which contributes to the hydrogels water absorption capabilities [39,41,42]. These hydrogels have demonstrated exceptional adsorption ability for heavy metals such as Pb(II), Cd(II), and Cu(II), owing to their highly configurable structure (e.g., through chemical, physical, enzymatical modifications) with the potential to target heavy metals [42–44]. This is mostly accomplished by modifications of their surface functional groups, which are easily replaceable, allowing them to potentially absorb some metals preferentially over others [44]. As a result, starch-based hydrogels may be an excellent low-cost adsorbent for heavy metals with multiple oxidation states, such as Cr.

In this work, starch-graft-itaconic acid hydrogels were investigated for the adsorption of the most abundant oxidation states of chromium in nature (i.e., trivalent chromium and hexavalent chromium). The considerations for this work are the experimental conditions, such as the pH and the volume of the solution, the properties of the hydrogels (e.g., surface functional groups), and the stable ionic forms of chromium. Batch adsorption experiments were conducted by constantly mixing oven-dried starch-graft-itaconic acid hydrogels dispersed in Cr(III) and Cr(VI) solutions at room temperature for 24 h. The concentration of chromium in solution was analyzed with inductively coupled plasma - optical emission spectroscopy.

The aim of this thesis is to broaden knowledge of the applications of starch-based hydrogels, which would further encourage the implementation of biobased hydrogels capable of selectively removing metals from polluted water.

## 1.2 Study objectives

## 1.2.1. General objective

Evaluate starch-graft-itaconic acid hydrogels for the adsorption of trivalent chromium Cr(III) and hexavalent chromium Cr(VI).

## 1.2.2. Specific objectives

- 1. To conduct a literature review on heavy metals that are stable in more than one oxidation state and their adsorption by biobased hydrogels.
- 2. To determine the water swelling capacity of starch-graft-itaconic acid hydrogels across a wide range of pH conditions.
- 3. To calculate the adsorption capacity of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels in a wide range of pH conditions.
- 4. To assess the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels under several volumes of chromium solution.
- 5. To estimate the binary adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels.

## 1.3 Hypothesis

Starch-graft-itaconic acid hydrogels are prospective biobased adsorbents able to selectively adsorb heavy metals in function of their oxidation state.

## 1.4 Thesis outline

This thesis is submitted in the form of two original papers published or submitted for publication in peer-reviewed scientific journals.

#### 2. The oxidation states of heavy metals and their adsorption behavior onto biobased

hydrogels – A review

Published in the International Journal of Environmental Science and Technology doi.org/10.1007/s13762-022-04632-8

## 2.1 Abstract

Heavy metal pollution in drinking water causes several health issues including permanent brain damage, cancer, and death. For this reason, extensive work has been dedicated to the removal of heavy metals from polluted waters. Nonetheless, little is known about the behavior of biobased hydrogels on the adsorption of heavy metals, and particularly heavy metals that are thermodynamically stable in more than one oxidation state. Depending on the oxidation state, the toxicity level of heavy metals can differ drastically. Therefore, this review aims to evaluate various biobased hydrogels for the adsorption of heavy metals by exploring the effect of several experimental conditions (such as the hydrogel weight, the initial concentration of the metal, and the adsorption time), the properties of the hydrogels and the metals. The determining factor in the adsorption efficiency is perhaps the interaction between the hydrogels and the metal, which is influenced by the physicochemical properties of the hydrogel (e.g., the surface area, surface functional groups, and point of zero charge), and the properties of the metal such as the molecular size and electronegativity.

## 2.2 Introduction

Heavy metals include metals and metalloids that are toxic to living organisms, regardless of their density [45,46]. Their presence in drinking water affects millions of people every year, namely because their ingestion leads to disorders such as paralysis and cancers, or damages to the nervous system by forming complexes with the functional groups (such as sulfhydryl and sulfur of cysteine and methionine) found inside living organisms' proteins and enzymes [47,48]. However, depending on the metals' oxidation state, their harmfulness might differ. For example, Cr(VI) intake causes damage to the liver, lungs, and stomach, whereas Cr(III) is considerably less toxic [45,49]. For this reason, according to the oxidation state of heavy metals, their presence in drinking water is of concern. A summary of the heavy metals, their thermodynamically stable oxidation states, and their corresponding maximum acceptable concentrations in drinking water are shown in Table 2.1

Heavy metal	Thermodynamically stable oxidation state in water	Maximum acceptable concentration/(mg/L)		
	As <sup>3+</sup>	T. 1.1		
As	As <sup>5+</sup>	Total As must be below 0.0		
Cd	$Cd^{2+}$	0.007		
C	Cr <sup>3+</sup>	No evidence of toxicity		
Cr	Cr <sup>6+</sup>	0.05		
C	Cu <sup>1+</sup>	N/A		
Cu	$Cu^{2+}$	2		
Ni	Ni <sup>2+</sup>	0.02		
Pb	Pb <sup>2+</sup>	0.005		
Zn	$Zn^{2+}$	5		

Table 2.1. Some heavy metals, their thermodynamically stable oxidation states, and their maximum acceptable concentration in drinking water [50], [51].

## N/A: not available.

Owing to the potential hazards of heavy metals to living organisms, vast research efforts have been deployed on their removal from aqueous solutions using reverse osmosis [52], membrane filtration [53,54], ion exchange [55–57], flotation [58], chemical precipitation [59,60], and adsorption [61–64] (Table 2.2). While membrane filtration and ion exchange are the two most common methods because of their efficiency, these processes are expensive [47]. Adsorption, on the other hand, is a low-cost, sustainable, and easy-to-implement process for the removal of heavy metals from aqueous solutions [65].

Heavy metal water treatment	Efficiency	Cost/(US\$/L water treated)	Reference
Reverse osmosis	30 % to 80 %	0.3	[15,66]
Membrane filtration (ceramic membranes)	95 %	3.21	[67]
Ion exchange	98 %	1E-5 to 4.5E-4	[15]
Flotation	70 % to 90 %	5E-6 to 2.5E-5	[65,68]
Chemical treatment	92 % to 99 %	0.38 to 1.22	[65,69]
Adsorption	83 % to 99 %	1E-5 to 2E-4	[15]

Table 2.2. Efficiency and estimated cost of the most common heavy metal water treatment processes.

Regarding adsorbents, much focus has shifted to materials that are harmless to the environment. Adsorbents such as biobased hydrogels are polymer networks made from natural resources, such as lignin [70], cellulose [71], and chitosan [72], with outstanding potential to adsorb heavy metals from contaminated waters [73,74]. For example, carboxymethyl cellulose-starch-gelatin based hydrogels adsorb Cu(II) [75], and grafted guar gum hydrogels are capable of adsorbing Cd(II) and Cu(II) [36]. This review seeks to provide a further understanding of the biobased hydrogels' adsorption capacity for heavy metals and heavy metals with more than one thermodynamically stable oxidation and the conditions favoring their selective adsorption (e.g., the monomers used during synthesis, the hydrogels' mass, the pH, the physicochemical properties of the hydrogels, and the properties of the heavy metals).

## 2.3 Biobased hydrogels for the adsorption of heavy metals

Hydrogels are cross-linked polymer chains forming a three-dimensional network that, upon contact with aqueous solutions, can expand hundreds of times their original volume by electrostatic repulsion between their surface functional groups and the ions of the aqueous system [76]. Such functional groups that comprise the hydrogels, including alcohol (R-OH), carboxyl (R-COOH), sulfonyl hydroxide (R-SO<sub>3</sub>H), amide (R-CONH<sub>2</sub>), and amine functional groups (R-NH<sub>2</sub>), are also a key component in the adsorption of heavy metals [77,78]. However, hydrogel synthesis usually

requires the use of toxic chemicals such as divinyl sulfone and epichlorohydrin [79]. Therefore, an alternative to these are biobased hydrogels, which are derived from biological or renewable sources such as starch, cellulose, or proteins [80,81].

However, biomasses, such as starch and cellulose, often lacks some functional groups that are essential for the adsorption of heavy metals [82]. Starch, for example, is an abundant biopolymer found in algae, animals, and plants that mainly contains O-H and C-H groups only [83,84]. As a consequence, starch is modified with phosphates, xanthates, sulfates, and carbamates to add such groups to its surface [85]. In contrast, protein-based hydrogels from collagen, keratin, and silk biomasses already contain functional groups such as carboxyl and amines that interact with heavy metals [86]. Therefore, according to the starting biomass for the production of monomers, the physicochemical properties of biobased hydrogels (e.g., mechanical strength, swelling capacity, and adsorption capacity for heavy metals) may vary significantly.

## 2.4 Factors influencing the adsorption of heavy metals onto biobased hydrogels

To further explore the relation between the biobased hydrogels' properties and the conditions that could be favorable in the selective adsorption for heavy metals, this section evaluates several relevant research works. To illustrate the effect of the contact time and hydrogel weight, Table 2.3 summarizes the experimental conditions and removal capacity for Cu(II) using biobased hydrogels. The contact time seems highly dependent on the kind of biobased hydrogel; some hydrogels can retain a considerable amount of heavy metal ions in a short amount of time (approximately 1 hour), while other hydrogels can take up to 24 hours. Regarding the hydrogel dry weight, it is evident that the biobased hydrogels' weight is independent from their adsorption capacity for heavy metals; for example, 50 mg of the corn starch-based hydrogels retained almost 20 mg/g more of Cu(II) than 100 mg of the eggshell-based hydrogels. In other words, the biobased hydrogels' capacity to adsorb heavy metals, such as Cu(II), is likely influenced by the biomass itself rather than the hydrogels' dry mass. This suggests the importance of their physicochemical properties, which are closely related to their surface functional groups. Such groups determine the hydrogels' surface charge, the kind of adsorption interaction that they have with the heavy metals, and the metals that the hydrogels are more likely to adsorb [87,88].

Biobased	Hydrogels'	Cu(II) initial	pН	Contact	Adsorption	Adsorption	Reference
hydrogel	dry	concentration/		time/h	capacity/(mg/g)	capacity	
	weight/mg	(mg/L)				rate <sup>a</sup> /(mg/g/h)	
Corn	50	200	5.5	24	49.3	2.05	[84]
starch							
Eggshell	100	200	6	1.5	34.48	22.98	[89]
Cellulose	20	200	4.7	8	~ 22	2.75	[90]
Sou	20	250	55	20	126.2	6.81	[01]
SUy	20	230	5.5	20	130.2	0.01	[91]
protein							
Chitosan	20	100	7	N/A	~ 300	N/A	[92]

Table 2.3. Biobased hydrogels for the adsorption of Cu(II).

<sup>a</sup> Linear approximation of the metal uptake.

N/A: not available.

The hydrogels' surface charge is determined by the ionic state of the functional groups since these groups may be positively charged, negatively charged, or neutral. This variation in the ionic charge of the functional groups is affected by the pH of the aqueous solution and the hydrogels' point of zero charge (PZC) [93]. For pH conditions below the hydrogels' PZC, their functional groups protonate (e.g., R-COO<sup>-</sup> and R-NH<sub>2</sub> groups protonate to form R-COOH and R-NH<sub>3</sub><sup>+</sup>, respectively) due to the predominance of H<sup>+</sup> ions [94,95]. Conversely, for pH conditions above the hydrogels' PZC, the functional groups deprotonate and favor the adsorption of positively charged metals [96]. This is illustrated in Table 2.4, where the greater adsorption under mild acidic conditions for Cr(III) is likely due to the predominantly negative ionic state of the biobased hydrogels' functional groups.

Biobased hydrogel	Hydrogels' surface functional groups	рН	Removal capacity/(mg/g)	Reference
Carboxymethyl cellulose	Carboxyl and amide	4.0	~ 15	[97]
Chitosan-sodium alginate	Carboxyl, hydroxyl, and amino	5.0	48	[98]
Chitosan-gelatin (C1G1)	Amide and amine	N/A	0.1	[99]
Graphene oxide/alginate	Carboxyl and hydroxyl	6.0	130	[100]

Table 2.4. Functional groups of various biobased hydrogels for the adsorption of Cr(III).

N/A: not available.

In general, these functional groups also determine the interaction mechanism, e.g., ion exchange, surface complexation, and electrostatic interactions in the adsorption of heavy metals. For instance, protonated imine groups and carboxyl groups are involved in electrostatic interactions [101]. This is illustrated in the study by Oh et al. (2021) [93], suggesting that the adsorption for Cr(III) is likely due to its electrostatic interaction with the hydrogels' carboxyl groups. For hydrogels with R-SO3-, R-N+(CH3)2, and R-N+(CH3)3 functional groups, the main adsorption mechanism is ion exchange [37]. For hydrogels with R-NH2 functional groups, the predominant heavy metal adsorption mechanism is surface complexation. Nonetheless, certain functional groups, such as R-COOH, can interact with heavy metals through any of these three mechanisms [37]. Consequently, functional groups containing O, N, or S atoms underline the adsorption interaction mechanism between the biobased hydrogels and the heavy metals (Table 2.5).

Biobased hydrogel	рН	Hydrogels' surface functional	Adsorption interaction mechanism	Adsorption capacity/(m g/g)	Reference
		groups			
Hemicellulose, poly O-	3.0	Amine	Electrostatic	22.8	[102]
acetyl					
galactoglucomannan-					
glycidyl					
methacrylate/(3-					
acrylamidopropyl)trime					
thylammonium chloride					
Gelatin	N/A	Hydroxyl	Electrostatic	12.3	[35]
Chitosan	4.5	Carboxyl and	Electrostatic	47.4	[95]
		amine			
Silk Sericin-	2.0	Amine.	Electrostatic	~ 170	[93]
Polyethyleneimine		carboxyl, and			[, -]
5		hydroxyl			
Cellulose-	2.0	Amine amino	Electrostatic	~ 185 9	[103]
polvethylenimine-	2.0	and hydroxyl		10017	[100]
quaternized cellulose					
Chitoson/oranga nacl a	4.0	Amina	Flastrastatic	11 50	[104]
acrylamide	4.0	Amilie,	Electrostatic	11.37	[104]
		bydroxyl			
		nyuloxyi			

Table 2.5. Adsorption capacity and reported adsorption mechanism of Cr(VI) onto various biobased hydrogels.

N/A: not available.

Such an interaction mechanism involving the metals and the surface functional groups of the hydrogels is further influenced by the metals' ionic charge, which may differ for each of the

oxidation states. For example, Cr(III) is stable as positively charged ions, while Cr(VI) is stable as oxyanions, e.g., chromate ( $CrO_4^{-2}$ ), dichromate ( $Cr_2O_7^{-2}$ ), hydrogen chromate ( $HCrO_4^{-}$ ), and hydrogen dichromate ( $HCr_2O_7^{-}$ ) [95]. This is depicted in chromium's Pourbaix diagram [94]. Hence, Cr(VI) oxyanions likely interact with the protonated amino groups via electrostatic interactions [103]. For this reason, the selective adsorption for heavy metals may be enhanced by considering the stable ionic state of the heavy metals and the biobased hydrogels' functional groups. Overall, this shows that the functional groups considerably influence the physicochemical properties of the hydrogels, the hydrogels' surface charge, the adsorption interaction, and the metals prone to being adsorbed.

Regarding the concentration of heavy metals, many works associate a positive relationship between their initial concentration and their adsorption uptake by biobased hydrogels. This is exemplified in the work by Duquette et al. (2020) [84]. They observed that the adsorption for Cu(II), Ni(II), and Zn(II) was higher with an increase in the initial concentration of the metal (i.e., the concentration gradient is the driving force for adsorption) and that the removal capacity is higher at lower metal concentrations. Accordingly, the uptake of heavy metals by biobased hydrogels is proportional to their initial concentration up to the saturation point of the hydrogels.

Similarly, there is also a direct correlation between the electronegativity of metal ions and their affinity for the hydrogels. Table 2.6 shows the electronegativity and the effective ionic radii of some metal ions, according to the coordination number. It was demonstrated in a competitive adsorption system evaluating Fe(III), Cu(II), Cr(III), and Zn(II) that their adsorption onto biobased hydrogels was linked with their electronegativity [105]. Therefore, the higher the electronegativity of the metal ions is, the higher their affinity is for positively charged adsorbents, regardless of the metals' oxidation state. For example, in the competitive adsorption for Pb(II), Cd(II), and Zn(II), these metals have a close direct relationship between their electronegativity and their affinity for tea residue-based hydrogels [106]. For this reason, the electronegativity of metals may provide insight into determining their adsorption behavior onto biobased hydrogels in competitive systems.

		Effective			
Metal	Electronegativity	Co	Reference		
		4	6	8	
Cd(II)	1.7	78	95	110	[107,108]
Co(II)	1.96	38	65	90	[108,109]
Cr(III)	1.66	N/A	61.5	N/A	[105,110]
Cr(VI)	3.37	26	44	N/A	[108,109]
Cu(I)	N/A	60	77	N/A	[108]
Cu(II)	1.90-1.98	57	73	N/A	[105,107–
					109]
Fe(II)	1.64	N/A	61	N/A	[108,109]
Fe(III)	1.83-2.20	N/A	55	N/A	[105,109,110]
Mg(II)	1.55	57	72.0	89	[107,108]
Mn(II)	1.66	66	67	96	[108,109]
Ni(II)	1.8-1.92	55	69.0	N/A	[106–108]
Pb(II)	1.92-2.33	98	120	129	[107–110]
Zn(II)	1.65	60	74.0	90	[106–108]

Table 2.6. Electronegativity and effective ionic radii (according to the coordination number) for some metals.

N/A: not available.

Moreover, the affinity of the metals toward biobased hydrogels is inversely correlated to the size of their ionic radii. For instance, in the competitive adsorption for Fe(III), Cr(III), and Pb(II), which have an ionic radii of 55, 61.5 and 120 picometers, respectively, Fe(III) had the highest relative amount adsorbed onto tea residue-derived gels [110]. Thus, the larger the ionic radii of the metal, the lower its affinity toward the hydrogels. This could be related to the steric

effect among the metals that are adsorbed on the hydrogels' surface. Another example is the case of soybean dreg-based hydrogels in the competitive adsorption of Zn(II), Fe(III), Cu(II), and Cr(III), where Fe(III) (55 picometers), which is the ion with the shortest effective radii in that multicomponent system, had the highest affinity toward the soybean hydrogel, while Zn(II) was adsorbed the least [105]. Furthermore, the ionic radii of metals vary according to their oxidation states. Therefore, from the electronegativity and ionic radii of heavy metals, their affinity for biobased hydrogels can be anticipated to a certain extent.

This behavior is further correlated with the Irving Williams series, which is based on the stability constant of the metals. It represents the order of stability of the chemical complexes that the metals form upon interacting with the adsorbent surface [111]. Based on the series, the stability order is as follows: Pd(II) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Fe(II) > Mn(II) > Mg(II) [107,112]. Hence, in theory, the complexes that Cu(II) forms with the hydrogels' functional groups are more stable than the Zn(II) ions. For example, in the competitive adsorption of Pb(II), Cu(II), Ni(II), and Zn(II) onto sago starch hydrogels, Cu(II) had the highest removal percentage, forming more stable chelate complexes than Ni(II) and Zn(II) [85]. Generally, in systems with multiple metals, metals with higher stability constants are adsorbed in higher quantities in comparison to metals with the least stable constants, according to the Irving Williams series.

On the other hand, the adsorption temperature is an independent variable. For example, metal adsorption may be favored at low temperatures, such as the adsorption of Cu(II) onto hydrogel composites of chitosan-g-poly(acrylic acid) embedded with cellulose [113], or their adsorption may be favored at high temperatures (endothermic process). This was shown by [114], where the adsorption of Cu(II) onto pectin-based hydrogels increased with temperature. Both previously mentioned studies tested the same metal, Cu(II), but the adsorption thermodynamic behavior was different, meaning that it was mostly influenced by the biomass. This could be due to the thermal stability of the biobased hydrogels.

Much of the current literature pays particular attention to two thermodynamic models (i.e., Langmuir and Freundlich) due to their simple determination [115–118]. The Langmuir model is a theoretical model that assumes uniform monolayer adsorption and excludes any interactions between the adsorbed metal ions [119]. The Freundlich isotherm, in contrast, is an empirical model that supposes multilayered adsorption onto a heterogeneous surface and considers the interaction

between the adsorbate ions [120]. Table 2.7 summarizes the adsorption capacity (ratio of the metal ions adsorbed per mass of hydrogel), isotherm model, and kinetics of various biobased hydrogels. In brief, the adsorption of the heavy metals onto hydrogels is primarily due to chemical interactions, confirmed by the better fit of the pseudo-second-order kinetics model. However, the isotherm models that best fit the adsorption experiments are particular for each system. The better fit of the Freundlich model could be due to the models' approach that considers heterogeneous surface coverage by the adsorbate.

Table 2.7. Adsorption isotherm and kinetics models in the adsorption of heavy metals onto biobased hydrogels.

Biobased	Metal <sup>a</sup>	Adsorption	Isotherm	Kinetic model	Reference
hydrogel		capacity/(mg/g)	model		
Cellulose	Cu(II), Pb(II), & Cd(II)	157, 393 & 289	Langmuir	Pseudo-second- order	[118]
Pectin	Cr(VI) & Pb(II)	825 & 913	Langmuir	Pseudo-second- order	[121]
Tea residue	Cr(III), Pb(II), & Fe(III)	206, 253, & 94	Freundlich	Pseudo-second- order	[110]
Cellulose	Cu(II)	130	Freundlich	Pseudo-second- order	[122]
Starch	Cu(II) & Pb(II)	2.06 mmol/g & 1.67 mmol/g	Freundlich	Pseudo-second- order	[123]
Soy protein	Cu(II)	90	Langmuir	Pseudo-second- order	[91]
Lignin	Cu(II)	1.17 mmol/g	Freundlich	Pseudo-second- order	[124]
Cassava starch	Cu(II)	76.6	Freundlich	N/A	[125]

<sup>a</sup> In all cases where more than one metal per hydrogel is discussed, it refers to batch adsorption experiments, with one metal ion type at a time. N/A: not available.

With respect to the adsorption kinetics, the adsorption rate of heavy metals varies according to their oxidation states. For the two stable oxidation states of Cr in water, Cr(III) and Cr(VI), each have a specific adsorption rate onto the hydrogels [126]. Therefore, even though it is essentially the same metal, its oxidation state ultimately determines its rate of adsorption. The rate constants for Cr(III) and Cr(VI) are 4.02E-3 g/(mg·min) and 2.14E-4 g/(mg·min), respectively, according to Dudu et al. (2015) [126]. For a period of 4 hours, the hydrogel removed up to 80% of Cr(VI) compared to only 15% removal for Cr(III). The higher percent removal for Cr(VI) could be due to the selective affinity for the functional groups embedded in the hydrogel structure. Hydrogels selectivity toward only one oxidation state of the heavy metals may maximize their adsorption capacity.

In summary, the vast research on biobased hydrogels is mostly focused on the adsorption of multiple heavy metals with their most stable oxidation state [127–130]. For example, the adsorption of Cu(II), Cd(II), and Ni(II) onto acrylic acid/acrylamide hydrogels [131]. Other authors tested the adsorption of Cu(II), Pb(II), and Cd(II) onto silk fibroin and polyethyleneimine composite hydrogels, and glucan/chitosan hydrogels [132,133]. Such works evaluate the adsorption capacity of hydrogels for several heavy metals in their most common oxidation state. For this reason, multicomponent adsorption studies evaluating the various oxidation states of heavy metals are promising research areas to explore.

This review of the literature outlined the trends of several works to gain better insight on the factors that can control the selective adsorption of heavy metals, such as the hydrogels' functional groups, the hydrogels' chemistry, some of the experimental conditions, and the interactions (ion exchange, electrostatic interaction, complexation, hydrogen bonding, hydrophobic interaction, acid-base interaction, coordination/chelation) that are involved in the adsorption of heavy metals onto the hydrogels [134]. Out of all the variables that influence the adsorption of the heavy metals, the pH and the functional groups that comprise the hydrogels' surface are the most determinant factors. The pH conditions for the adsorption of heavy metals can be optimized based on the hydrogels' PZC.

## 2.5 Conclusions

Heavy metal pollution in drinking water is a prevalent problem that claims the lives of thousands of people around the world every year. For example, arsenic-contaminated waters cause health damages to approximately 150 million people [95]. Promising materials with the potential to adsorb heavy metals from polluted waters are biobased hydrogels, which are hydrophilic polymer networks from biomasses such as starch, proteins, and cellulose. This work contributes to the understanding of the adsorption parameters that can maximize the adsorption of heavy metals using biobased by considering the interactions between the hydrogel and the heavy metals. These interactions are primarily influenced by the physicochemical properties of the hydrogels (e.g., the surface functional groups and the PZC) and the properties of the heavy metals, such as the molecular size and electronegativity. Furthermore, some experimental conditions, such as the pH, initial concentration of the metal, hydrogel weight, and biomass of the hydrogels are also evaluated. Generally, among these experimental conditions, the pH is perhaps the most significant on the overall performance of the adsorption for heavy metals onto the biobased hydrogels due to its influence over the ionic state of the hydrogels' surface functional groups. Therefore, by considering the functional groups of the biobased hydrogels, the pH has the potential to improve the selective adsorption of heavy metals.

## 3. Connecting statement

The literature review highlighted the relevance of assessing the adsorption of heavy metals stable in more than one oxidation state by biobased hydrogels, as well as the factors involved in the adsorption process, such as the experimental conditions, hydrogel physicochemical properties, and heavy metal properties. Five major facts emerged from this literature review:

- 1. Aqueous heavy metal adsorption is frequently studied for different metals with the same oxidation state. Most research evaluates the adsorption of several metals with the same oxidation state (e.g., Ni(II), Cd(II), Pb(II), Cu(II)). However, the properties and toxicity of heavy metals may vary drastically depending on their oxidation state.
- 2. The functional groups of hydrogels are strongly correlated with their selectivity for aqueous heavy metals. According to the literature, functional groups containing elements such as oxygen, sulfur, or nitrogen may interact with metal ions.
- 3. The majority of the experimental variables reported for aqueous metal adsorption have fairly predictable outcomes. Vast research examines similar experimental variables, but many of them, such as the initial concentration of aqueous metals and test time, produce consistent results.
- 4. Aqueous heavy metals may be thermodynamically stable in more than one ionic form, depending on the pH and redox potential (Eh) of the solution, illustrated in the Pourbaix diagrams. This diagram is useful to determine the ionic charge of aqueous metals and providing a plausible explanation for their adsorption behavior by biobased hydrogels.

The electronegativity and molecular size of aqueous metals do provide insight into their adsorption behavior. The increase in metals molecular size can lead to higher steric effects between them, therefore, inhibiting their interactions with the surface of hydrogels. Furthermore, the molecular size of the same metal, such as chromium, varies depending on its ionic form (e.g.,  $HCrO_4^-$ ,  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$ ).

In the next chapter, starch-graft-itaconic acid hydrogels are tested in batch for the adsorption of Cr(III) and Cr(VI), evaluating the effect of chromium solution pH and volume.

## 4. Selective adsorption of Cr(III) over Cr(VI) by starch-graft-itaconic acid hydrogels

Submitted for publication in the Journal of Hazardous Materials Advances

## 4.1 Abstract

This work investigates the applicability of starch-graft-itaconic acid hydrogels in the adsorption of Cr(III) and Cr(VI) in single- and binary-component systems. Batch adsorption studies were conducted at room temperature for 24 h using 0.1 g of hydrogels to explore the effect of pH, volume, and the binary system of Cr(III) and Cr(VI) solutions with a starting concentration of 100 mg/L. At pH 8.0, the adsorption of Cr(III) and Cr(VI) was up to 14.13 mg/g  $\pm$  0.42 mg/g and 1.11 mg/g  $\pm$  0.36 mg/g, respectively, validating that it is indeed possible to selectively adsorb one valence over another. This is mostly owing to the starch-graft-itaconic acid hydrogel functional groups (e.g., carbonyl, carboxyl), that depending on the pH, can become positively charged, negatively charged, or neutrally charged, contributing to this selectivity. Furthermore, because the stable ionic forms of Cr(III) are similarly pH dependent, the major adsorption mechanisms for Cr(III) by starch-graft-itaconic acid hydrogels may be through electrostatic interactions, ion exchange, and surface complexation.

Keywords: biobased polymers; wastewater treatment; heavy metals; metal removal

## 4.2 Introduction

Every year, millions of people worldwide are affected by chromium-polluted water, which is both an environmental and human health concern [135]. Chromium (Cr) reaches groundwater bodies mostly through anthropogenic activities such as ore refining, electroplating, and leather tanning [136]. The most frequent forms of aqueous chromium are trivalent chromium Cr(III) and hexavalent chromium Cr(VI), which may cause skin rashes or even cancers [7,49,137]. The maximum permitted content of total Cr (i.e., all forms of Cr) in drinking water should be less than 0.1 mg/L, and for the various industrial effluents, it must be less than 1.71 mg/L on average per month, according to United States Environmental Protection Agency (USEPA, 2021) [138]. However, the total Cr concentrations in some industrial effluents, such as those from the tannery sector, can range from 0.7 mg/L to 345 mg/L [10].

As a result, several efforts have been made to develop an effective method for removing Cr from water, including adsorption, membrane filtration, electrochemical treatments, and microbial treatments [139]. Adsorption is frequently recognized as an efficient, cost-effective, and

straightforward process for this purpose [140]. Common adsorbents for Cr include inorganic materials (e.g., carbonaceous, minerals, metal oxides), such as graphene, clays, zeolites, and silicious materials; polymer-based materials (e.g., synthetic and natural polymers, ion-imprinted polymers [141–143]); composite materials (i.e., mixture of organic and inorganic materials); and waste or by-products of animals, agriculture, and industry (chicken feathers, eggshells, nutshells, fly ash) [21,22,144]. Carbon-based nanomaterials such as functionalized carbon nanotubes [145] and multiwalled carbon nanotube composites [146] have attracted much attention for the adsorption of Cr due to their large surface area, porosity, chemical composition, and high stability [147,148]. For example, chitosan-coated iron oxide nanoparticles are superparamagnetic materials capable of adsorbing Cr(VI) at acidic pH values [149]. Furthermore, materials such as sulfidemodified nanoscale zerovalent iron, which is reactive and stable, have demonstrated great adsorption performance for Cr(VI) [150]. However, environmental sustainability (i.e., their hazardousness makes their ultimate disposal difficult), cost, and synthesis time are limiting considerations for their widespread implementation [18,148]. The cost of industrial adsorbent manufacture is rarely disclosed in research studies, although one work does state the cost of activated carbon. According to Mariana et al. (2021) [151], the chemical and physicochemical procedures for generating activated carbon need a total fixed capital investment of USD 6,320,000 and an annual operating cost of USD 2,570,000. (2021). Additionally, the cost of the adsorbent depending on its adsorption ability must also be evaluated [152].

Some research has indicated that combining multiple materials as one adsorbent can boost metal adsorption, which may help mitigate some of the limitations previously mentioned. For example, one study showed that combining nanoscale zero-valent iron with Fe<sub>3</sub>O<sub>4</sub> resulted in a 47 % removal increase for the adsorption of Cr(VI) as compared to either material alone [153]. In another study, nanocomposite materials were synthesized by combining graphene oxide, manganese dioxide nanowires, iron oxide nanoparticles, and polypyrene for the adsorption-reduction of Cr(VI) [154]. The addition of metals such as zero-valent copper has also been proven to increase the removal of Cr(VI) when compared to nanoscale zero-valent iron alone [155]. However, there are several concerns with these processes involving the reduction of Cr(VI) to Cr(III) and its subsequent adsorption. For example, the functional groups and active adsorption sites on the adsorbents are permanently consumed [144]. Therefore, their adsorption efficacy for consecutive adsorption cycles is significantly reduced. Furthermore, the catalytic reduction of

Cr(VI) may produce carbon dioxide as a by-product, which is damaging to the environment [155]. Lastly, the reduced Cr(VI) (i.e., Cr(III)) is frequently difficult to remove from such adsorbents, and Cr(III) buildup may be ecologically hazardous [18,144].

In contrast, biobased polymers, such as those derived from cellulose, chitosan, and lignin, have several benefits over the majority of materials previously addressed, including their biocompatibility, abundance, cost-effectiveness, and renewable nature [144]. These polymers are promising materials for the adsorption of Cr due to their surface chemical composition, which may include functional groups composed of nitrogen, oxygen, and sulfur (e.g., hydroxyl, carboxyl, epoxy, phosphoryl, amine, and sulfonic acid) that function as binding sites for heavy metal adsorption [18,37]. For example, under basic pH conditions, carboxyl (R-COOH) and hydroxyl groups (R-OH) donate their hydrogen atoms and become negatively charged groups, R-COO<sup>-</sup> and R-O<sup>-</sup>, respectively, which confer their capacity to interact with positively charged metal ions [37]. Other functional groups, such as sulfonic acid groups (R-SO<sub>3</sub>H) (which generate sulfonate ions, R-SO<sub>3</sub><sup>-</sup>), are unaffected by the pH of the solution and therefore interact with positively charged ions over a wide range of pH values [37].

Another significant advantage of these martials is that their surface chemistry can be tuned to include functional groups capable of selectively removing certain heavy metals through physical (e.g., addition of organic and inorganic materials) and chemical modifications (e.g., crosslinking, surface grafting) [144,156]. For example, biobased hydrogels are three-dimensional polymer networks made of nontoxic, natural, and renewable materials that swell in aqueous solutions due to electrostatic repulsions between their numerous hydrophilic functional groups (e.g., R–COOH, R–OH) [73,157]. The swelling of the hydrogel structure exposes their surface functional groups, which also enhances heavy metal adsorption [158], such as Cu(II) [131], Cd(II) [36], and Pb(II) [159].

Starch is a low-cost, abundant, and biodegradable biopolymer that, in the form of hydrogels, is notable for its hydroxyl functional groups, which may be replaced by other functional groups to potentially target the selective adsorption of heavy metals [44]. This is done by adjusting their synthesis parameters, such as grafting degree, reagents, and crosslinking [160]. Starch-based hydrogels have been studied for the adsorption of several divalent ions (e.g., Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)), as commonly done for various adsorbents [76,160,161]. However, the behavior of

starch-based hydrogels for the selective adsorption of Cr remains unknown. As a result, in this work, starch-graft-itaconic acid hydrogels are investigated for the adsorption of Cr(III) and Cr(VI) in single- and binary-component systems, evaluating the effects of Cr solution pH and volume. The outcome of this study is expected to further contribute to the removal of Cr from contaminated water using innocuous natural resources such as corn starch in the form of biobased hydrogels and pave the way toward more selective hydrogel formulations.

#### 4.3 Materials and methods

## 4.3.1. Materials

All the reactants were used as received. Starch from corn ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (99.0 % purity), itaconic acid (HO<sub>2</sub>CCH<sub>2</sub>C(=CH<sub>2</sub>)CO<sub>2</sub>H) (99 % purity), citric acid (HOC(COOH)(CH<sub>2</sub>COOH)<sub>2</sub>) (99.5 % purity), chromium chloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O) (96 % purity), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) (99 % purity), and sodium hydroxide (NaOH) (98 % purity) were purchased from Sigma–Aldrich Co. LLC, USA. A 70 % denatured ethanol solution and nitric acid trace metal grade solution (HNO<sub>3</sub>) (86 % purity) were purchased from Thermo Fisher Scientific (Fair Lawn, NJ, USA). The hydrogels and all the solutions were prepared using distilled water with a specific resistance of 18.2 MΩ · cm at 25 °C.

#### 4.3.2. Synthesis of starch-graft-itaconic acid hydrogels

The synthesis of starch-graft-itaconic acid hydrogels was adapted from the procedure reported by Duquette et al. (2020) [84]. Figure 4.1 shows a schematic representation of the procedure. In a 250 mL flat bottom flask, 6.0 g of corn starch (biobased polymer backbone), 6.0 g of citric acid (crosslinker), and 60 mL of distilled water (solvent) were added. This solution was heated in an oil bath at 90 °C and constantly stirred at 300 rpm for 45 min. Then, the temperature was lowered to 70 °C, and 4.5 g of potassium persulfate (free radical initiator) was added. After stirring for 5 min, 60 mL of a solution containing 12.0 g of itaconic acid (grafting reagent) and 3.66 g of sodium hydroxide (neutralizing reagent) (50 % neutralized) was added. The solution was stirred for 15 min, and thereafter, the flask was maintained at 70 °C for 3 h without stirring. Next, the solution was poured onto a petri dish and air-dried inside the fume hood for approximately 72 h. Then, the air-dried hydrogels were soaked in distilled water for 24 h. Subsequently, the material was rinsed multiple times with a solution of equal parts ethanol and water (removal of leachable components) until a clear filtrate solution was obtained. Finally, the hydrogels were dried at 40 °C in an oven

until a constant mass was obtained. The hydrogels were then reduced to a powder form using a mortar and pestle. The physical and chemical characterization of these starch-graft-itaconic acid hydrogels using ATR-FTIR, scanning electron microscopy, and thermogravimetric analysis has already been reported in a previous study [84].



Figure 4.1. Schematic illustration of starch-graft-itaconic acid hydrogel synthesis.

## 4.3.3. Point of zero charge of starch-graft-itaconic acid hydrogels

The point of zero charge is the pH value at which the surface concentration of negative and positive ions is equal, indicating that the charge on the surface is zero. In contrast, the isoelectric point is the pH at which a surface's zeta potential equals zero, which is associated with the materials' acidic and basic functional groups [162]. Only the point of zero charge was measured in this study. The procedure was adapted from the work by Munim et al. (2020) [163]. The tests were performed in triplicate, and average results are presented in this work. The point of zero charge of starch-graft-itaconic acid hydrogels was determined using 0.1 g of oven-dried hydrogels dispersed in 50 mL of distilled water at room temperature at pH 2.0, 4.0, 6.0, 8.0, and 10.0 (considered as the initial pH) in 50 mL conical centrifuge tubes. The pH was measured using a pH meter (Thermo Electron Orion 710A). The pH of distilled water was adjusted with 0.5 M NaOH and 4 M HNO<sub>3</sub>. After mixing the samples in a 360° vertical rotating mixer for 24 h, they were centrifuged at 3,300 rpm for 20 min (Beckman Allegra X-12R refrigerated benchtop centrifuge). Thereafter, the pH of the supernatant water was measured, and this was considered the final pH. The point of zero charge of starch-graft-itaconic acid hydrogels was calculated by plotting  $\Delta$ pH (final pH – initial pH) as a function of initial pH.

#### 4.3.4. Effect of the pH on the water retention capacity of starch-graft-itaconic acid hydrogels

The procedure to determine the hydrogels' water retention capacity was adapted from Lai et al. (2020) [164]. The tests were performed in triplicate, and average results are presented in this work. The effect of the pH was studied in distilled water at pH 2.0, pH 6.0, pH 8.0, and pH 10.0, which was adjusted with 0.5 M NaOH and 4 M HNO<sub>3</sub>. Additionally, distilled water without pH adjustment was also tested (pH of approximately 5.0). In 50 mL conical centrifuge tubes, 0.1 g of oven-dried hydrogels were dispersed in 50 mL of distilled water at room temperature at each pH value. The samples were constantly mixed in a 360° vertical rotating mixer for 24 h and thereafter centrifuged (3,300 rpm for 20 min). The supernatant was decanted, and the mass of the swollen hydrogels was recorded. The mass of distilled water adsorbed per mass of dry hydrogel was obtained with Equation 1, where  $m_s$  is the mass of the swollen hydrogels in g, and  $m_d$  is the mass of the oven-dried hydrogels in g.

Water retention capacity 
$$=\frac{m_s - m_d}{m_d}$$
 1

## 4.3.5. Batch adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels

The most widely researched variables for metal adsorption by hydrogels are the initial pH of the solution, the starting concentration of the metal solution, the test duration, and the temperature [165–167]. Nonetheless, for some of these variables, the pattern of the findings is rather predictable. For example, the adsorption of metals by hydrogels tends to rise as the initial concentration of the metal solution and test duration increase [156,168–170]. In contrast, for the temperature and initial pH of the metal solution, the findings vary depending on the system. For example, Cr(III) adsorption by carboxymethyl cellulose-based membranes was favored by a drop in temperature (i.e., an exothermic process) [97], but Cr(III) adsorption by graphene oxide/alginate hydrogel membranes was endothermic [100]. Other examples include the endothermic adsorption of Cr(VI) by chitosan-based and carboxymethyl cellulose/polyethylenimine-based hydrogels [101,171] but exothermic adsorption by sodium lignosulfonate-based hydrogels [172]. Therefore, the thermodynamics appear to be determined by the hydrogels rather than the adsorbate. The scope of this work, however, was to conduct the experiments exclusively at room temperature. As a result, the influence of the initial pH of the Cr(III) and Cr(VI) solutions, as well as the effect of the Cr solution volume (i.e., ratio of hydrogels to volume of chromium solution), were investigated. The mass of oven-dried starch-graft-itaconic acid hydrogels and initial concentration of the Cr(III) and Cr(VI) solutions were set to 0.1 g and 100 mg/L, respectively.

The sources of Cr(III) and Cr(VI) were CrCl<sub>3</sub>·6H<sub>2</sub>O and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, respectively. To prevent cross-contamination in the preparation of the solutions, all glassware were rinsed at least 15 times with distilled water, thereafter with acetone, and finally dried at 40 °C in an oven. Stock solutions (2,000 mg/L) of Cr(III) and Cr(VI) were prepared by dissolving 21.35 g of CrCl<sub>3</sub>·6H<sub>2</sub>O and 11.32 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, respectively, in 2 L volumetric flasks. Working solutions of Cr(III) and Cr(VI) at 100 mg/L were obtained by dilution of the stock solution. Batch adsorption tests were carried out in triplicate, and average results are presented in this work.

Considering that K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is hazardous, the process for safely preparing the Cr(VI) solution is described. A certain amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was poured into a pre-weighed conical centrifuge tube. The tube was then wiped clean with disposable wipes. The worn pair of hand gloves were thrown away in a solid waste container box lined with a plastic bag. Wearing a new pair of hand gloves, the tube containing  $K_2Cr_2O_7$  was weighed. This process was repeated until the necessary weight of  $K_2Cr_2O_7$  was obtained. Next, distilled water was added to the tube, and with a plastic funnel, the solution of the tube was poured into a 2 L volumetric flask. The tube was rinsed with distilled water at least ten times, and the solution was poured into the volumetric flask. Then, the tube and plastic funnel were placed in the solid waste box. Thereafter, distilled water was added up to the graduated line of the volumetric flask, and the solution was stored in a white plastic bottle. The volumetric flask was rinsed with distilled water multiple times, and the liquid waste was disposed of in a yellow plastic tight head waste container.

## 4.3.5.1. Effect of the Cr solution pH on the adsorption of Cr(III) and Cr(VI) by starch-graftitaconic acid hydrogels

The initial pH values of the Cr(III) and Cr(VI) solutions were  $3.1 \pm 0.1$  and  $4.5 \pm 0.2$ , respectively. The pH was adjusted to 2.0, 4.0, 6.0, 8.0, and 10.0 using 0.5 M NaOH and 4 M HNO<sub>3</sub>. In a 50 mL conical centrifuge tube, 0.1 g of oven-dried hydrogels were dispersed in 50 mL of Cr(III) or Cr(VI) solutions at each pH value. The tubes were mixed at room temperature in a 360° vertical rotating mixer for 24 h and then centrifuged (3,300 rpm, 20 min). A 5 mL aliquot was taken from the supernatant to determine the concentration of Cr in the solution.

This study tests the adsorption of Cr under strong acidic conditions (i.e., at pH 2.0) due to the plethora of articles that mention a favorable adsorption of Cr under acidic pH values, such as the works by Samrot et al. (2019) [149], Lu et al. (2017) [146], and Farooqi et al. (2021) [155]. Liu et al. (2018) [154] discussed that at acidic pH values the adsorbents surface protonates leading to a higher uptake of Cr(VI) than at basic pH values. This is demonstrated in another study which found that the adsorption of Cr(VI) by nZVI composites was favorable at pH 3.0 [153]. Farooqi et al. (2021) [155] mentioned that the forms of Cr(VI) at pH values below 2.0 (i.e., HCrO<sub>4</sub>) is more reactive than for the forms of Cr(VI) at pH values above 2.0, therefore the reduction of Cr(VI) to Cr(III), and subsequent adsorption, is more likely under acidic conditions.

## 4.3.5.2. Effect of the Cr solution volume on the adsorption of Cr(III) and Cr(VI) by starchgraft-itaconic acid hydrogels

In 50 mL conical centrifuge tubes, 0.1 g of oven-dried starch-graft-itaconic acid hydrogels were dispersed in 15 mL, 35 mL, or 50 mL of Cr(III) and Cr(VI) solutions without adjusting their pH. The tubes were constantly mixed in a 360° vertical rotating mixer at room temperature for 24 h.

Thereafter, the tubes were centrifuged at 3,300 rpm for 20 min. A 5 mL aliquot was then taken from the supernatant to determine the concentration of chromium.

# 4.3.5.3. Binary component adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels

In 50 mL conical centrifuge tubes, 0.1 g of oven-dried starch-graft-itaconic acid hydrogels were dispersed with a mixture containing either 15 mL of Cr(III) and 35 mL of Cr(VI), 25 mL of Cr(III) and 25 mL of Cr(VI), or 35 mL of Cr(III) and 15 mL of Cr(VI) solutions, without adjusting the pH. The tubes were mixed in a 360° vertical rotating mixer at room temperature for 24 h. Then, the hydrogels were separated from the solution by centrifugation at 3,300 rpm for 20 min. A 5 mL aliquot was taken from the supernatant to determine the concentration of chromium in the solution.

#### 4.3.6. Analysis of the concentrations of Cr(III) and Cr(VI) in aqueous solution

In 15 mL autosampler tubes, a 1 mL supernatant aliquot was diluted with 1 mL trace metal grade HNO<sub>3</sub>. The tubes were heated to 95 °C for 1 h in a *Digi*PREP digestion block system (SCP Science *Digi*PREP Jr). Once the tubes cooled, their volume was brought to 10 mL with distilled water (1 to 10 dilution factor). Then, the samples were analyzed using ICP–OES (Thermo 6500 Dual View, Thermo Fisher Scientific, US). The calibration curve was made from 0.1 ppm to 100 ppm (i.e., blank, 0.1 ppm, 1 ppm, 10 ppm, and 100 ppm) using NIST traceable standards. The total concentration of Cr in the solution determined by ICP–OES was adjusted by the dilution factor (1:10) to obtain the actual concentration. It is worth mentioning that ICP-OES detects the total amount of Cr only – it is not selective to a particular oxidation state. The results presented in this work are the average of both Cr emission peaks at 267 nm and 283 nm.

The hydrogels' adsorption capacity of Cr(III) and Cr(VI),  $q_e$  in mg/g, was calculated using Equation 2 [95], where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations of Cr in mg/L, respectively, V is the volume of solution in L, and m is the mass of the oven-dried hydrogels in g. The removal efficiency percentage (R, %) of Cr from the solution by the hydrogels was calculated with Equation 3 [95]. The analysis of the data, t-test, and one-way ANOVA (analysis of variance) were performed using Microsoft Excel (version 16.66.1). For p-values less than 0.05, the difference was considered significant.

$$q_e = \left(\frac{C_0 - C_e}{m}\right) \cdot V \tag{2}$$

$$R, \% = \left(\frac{C_0 - C_e}{C_0}\right) \cdot 100$$

## 4.4 Results and discussion

## 4.4.1. Point of zero charge of starch-graft-itaconic acid hydrogels

The pH at which  $\Delta$ pH crosses the zero y-axis is the hydrogels' point of zero charge (pH<sub>PZC</sub>) (shown in Figure 4.2) [173]. The pH<sub>PZC</sub> of starch-graft-itaconic acid hydrogels is at pH 4.0. For pH values lower than the pH<sub>PZC</sub>, the surface charge of starch-graft-itaconic acid hydrogels is primarily positively charged. In contrast, for pH levels exceeding the pH<sub>PZC</sub>, the surface charge is predominantly negatively charged. Therefore, at pH 2.0 and pH 4.0 the hydrogels may have a slightly positively charged surface. However, considering that the  $\Delta$ pH at these two initial pH values is 0.15 and 0.17, respectively, the surface charge at these two pH values may fluctuate between positively charged and neutrally charged.



Figure 4.2. Point of zero charge of starch-graft-itaconic acid hydrogels. Error bars with 95 % confidence level from three replicates.

This fluctuation in the surface charge of starch-graft-itaconic acid hydrogels with the pH of the solution is linked to their surface functional groups [174]. The functional groups may switch

their ionic state to positively charged, negatively charged, or neutrally charged groups. At pH values lower than the hydrogels' pH<sub>PZC</sub>, functional groups tend to protonate and are more akin to negatively charged metal ions. Conversely, deprotonation of functional groups occurs at pH levels above the hydrogels' pH<sub>PZC</sub>, which favors the adsorption of positively charged metal ions. For example, hydroxyl groups (R-OH) and carboxyl groups (R-COOH), the primary functional groups of starch-graft-itaconic acid hydrogels (Figure 4.3), may deprotonate to form (R-O<sup>-</sup>) and (R-COO<sup>-</sup>). This process is highly dependent on the pH of the solution and the pH<sub>PZC</sub> of starch-graft-itaconic acid hydrogels.



Figure 4.3. Chemical structure of starch-graft-itaconic acid hydrogels. Adapted from Duquette et al. (2020) [84].

4.4.2. Effect of pH on the water retention capacity of starch-graft-itaconic acid hydrogels The hydrogels had a similar water retention capacity from pH 5.0 to pH 10.0, as illustrated in Figure 4.4. At pH 10.0, the hydrogels had the highest water retention (58.16 mg/g  $\pm$  1.19 mg/g), which may be attributable to, among other factors, the hydrophilic functional groups of the hydrogels, for example, R-OH [76]. In contrast, under acidic conditions (pH 2), the water retention capacity of starch-graft-itaconic acid hydrogels was greatly decreased (7.64 mg/g  $\pm$  0.22 mg/g). This may be due to a greater fraction of hydrogen ions (H<sup>+</sup>) at acidic pH levels that interact with the functional groups of the hydrogels, reducing their swelling ability. The primary mechanism by which hydrogels expand or swell is the electrostatic repulsion between their functional groups (R-COO<sup>-</sup>), for example, protonate to R-COOH groups, which are neutrally charged, limiting the expansion of the hydrogel polymer network. The hydrogel structure also swells due to capillarity through its porous structure [35].



Figure 4.4. Effect of pH of distilled water on the water retention capacity by starch-graft-itaconic acid hydrogels. Error bars with 95 % confidence level from three replicates.

# 4.4.3. Single-component adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels

The results are presented in Table 4.1 and Table 4.2, and it is graphically shown in Figure 4.5. From these results it can be inferred that there was a negligible uptake of Cr(VI) at pH 4.0 (-1.15 mg/g  $\pm$  0.49 mg/g) and at pH 6.0 (-0.05 mg/g  $\pm$  0.5 mg/g). In fact, there was no significant difference in the adsorption of Cr(VI) (*p*-value = 0.1895) between the means of all pH values. The negative adsorption results reported in Figure 4.5 may partly be due to the hydrogels absorbing a certain volume of water while the amount of Cr(VI) in the system remained almost constant. Therefore, the final concentration of Cr(VI) per volume of solution increased, resulting in a negative value. At pH 2.0, 8.0 and 10.0, the adsorption of Cr(VI) were 0.61 mg/g  $\pm$  0.73 mg/g, 1.11 mg/g  $\pm$  0.36 mg/g, and 0.45 mg/g  $\pm$  0.88 mg/g, respectively. Several reasons, including the ionic state of the functional groups on the surface of the starch-graft-itaconic acid hydrogels and the stable ionic form of Cr, are partially responsible for such low uptake of Cr(VI). For example, cationic functional groups, such as amine and imine groups, which are lacking in the network of starch-graft-itaconic acid hydrogels, are reported to be involved in the adsorption of Cr(VI) [16,95,101,175].

Sample	Cr267/ ppm	Cr283/ ppm	Average (Cr267, Cr283)/ppm	Average (Cr267, Cr283 * DF 1:10)/ppm	Average of replicates/ppm	q <sub>e</sub> /(mg/g)	SD	95 % Confidence	Standard error	Average q <sub>e</sub> /(mg/g)	Removal efficiency
Unadjusted pH-1	9.75	10.05	9.90	99.0	97.7	2.2	0.70	0.79	0.40	$2.91\pm0.4$	5.64%
Unadjusted pH-2	9.47	9.77	9.62	96.2		3.6					
Unadjusted pH-3	9.63	9.92	9.78	97.8		2.9					
pH 2.0-1	9.79	10.11	9.95	99.5	99.9	2.0	0.41	0.46	0.24	$1.78\pm0.23$	3.45%
pH 2.0-2	9.75	10.11	9.93	99.3		2.1					
pH 2.0-3	9.90	10.26	10.08	100.8		1.3					
pH 4.0-1	9.64	9.98	9.81	98.1	95.4	1.7	1.35	1.53	0.78	$3.07\pm0.77$	6.05%
pH 4.0-2	9.10	9.44	9.27	92.7		4.4					
pH 4.0-3	9.37	9.73	9.55	95.5		3.0					
рН 6.0-1	8.66	9.06	8.86	88.6	88.2	2.3	0.54	0.61	0.31	$2.53\pm0.31$	5.43%
рН 6.0-2	8.52	8.88	8.70	87.0		3.1					
рН 6.0-3	8.71	9.10	8.91	89.1		2.1					
pH 8.0-1	6.10	6.39	6.25	62.5	60.9	13.3	0.73	0.82	0.42	$14.13\pm0.42$	31.72%
pH 8.0-2	5.83	6.09	5.96	59.6		14.8					
pH 8.0-3	5.92	6.18	6.05	60.5		14.3					
pH 10.0-1	8.52	8.90	8.71	87.1	86.4	2.3	0.40	0.46	0.23	$2.7\pm0.23$	5.90%
pH 10.0-2	8.45	8.84	8.65	86.5		2.7					
pH 10.0-3	8.34	8.76	8.55	85.5		3.1					

Table 4.1. Effect of pH on the adsorption of Cr(III) by starch-graft-itaconic acid hydrogels.

## DF: dilution factor

SD: standard deviation

Table 4.2. Effect of pH on the adsorption of Cr(VI) by starch-graft-itaconic acid hydrogel
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Sample	Cr267/ ppm	Cr283/ ppm	Average (Cr267, Cr283)/ppm	Average (Cr267, Cr283 * DF 1:10)/ppm	Average of replicates/ppm	q <sub>e</sub> /(mg/g)	SD	95 % Confidence	Standard error	Average q <sub>e</sub> /(mg/g)	Removal efficiency
Unadjusted pH-1	8.84	9.31	9.08	90.8	93.1	2.6	1.30	1.48	0.75	$1.45\pm0.75$	3.03%
Unadjusted pH-2	9.02	9.50	9.26	92.6		1.7					
Unadjusted pH-3	9.32	9.86	9.59	95.9		0.0					
pH 2.0-1	8.87	9.36	9.12	91.2	91.6	0.9	1.28	1.45	0.74	$0.61\pm0.73$	1.33%
pH 2.0-2	8.70	9.17	8.94	89.4		1.8					
рН 2.0-3	9.19	9.69	9.44	94.4		-0.8					
pH 4.0-1	9.19	9.70	9.45	94.5	92.6	-2.1	0.86	0.98	0.50	$\textbf{-1.15}\pm0.49$	-2.55%
pH 4.0-2	8.99	9.46	9.23	92.3		-1.0					
pH 4.0-3	8.86	9.35	9.11	91.1		-0.4					
рН 6.0-1	8.63	9.12	8.88	88.8	90.2	0.6	0.87	0.99	0.50	$\textbf{-0.05} \pm 0.5$	-0.13%
рН 6.0-2	8.95	9.47	9.21	92.1		-1.0					
рН 6.0-3	8.74	9.18	8.96	89.6		0.2					
pH 8.0-1	8.30	8.71	8.71	87.1	88.5	1.8	0.62	0.71	0.36	$1.11\pm0.36$	2.46%
рН 8.0-2	8.50	8.89	8.89	88.9		0.9					
рН 8.0-3	8.56	8.95	8.95	89.5		0.6					
pH 10.0-1	8.61	9.00	8.81	88.1	89.1	1.0	1.54	1.74	0.89	$0.45\pm0.88$	1.02%
pH 10.0-2	9.06	9.45	9.26	92.6		-1.3					
pH 10.0-3	8.47	8.86	8.67	86.7		1.7					

DF: dilution factor

SD: standard deviation



Figure 4.5. Effect of pH on the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels. Error bars with 95 % confidence level from three replicates. \*At pH 10, some precipitation of Cr(III) occurred; therefore, the results are partly due to adsorption.

In contrast, the adsorption of Cr(III) was up to 14.13 mg/g  $\pm$  0.42 mg/g at pH 8.0, significantly higher than that observed for all other pH conditions, but it should be noted that at pH 6.0 and pH 8.0, the Cr(III) solution was turbulent. Starch-graft-itaconic acid hydrogels adsorbed Cr(III) throughout a wide pH range, from acidic (pH 2.0) to fairly basic (pH 10.0) conditions. These findings indicate that starch-graft-itaconic acid hydrogels have promising use in the selective adsorption of Cr(III) from wastewaters of various industries. For example, effluents from the tannery industry (which is known to contain significant levels of Cr(III)) usually have pH values of around 4.0 [176], but another study found that the pH of effluents from a local tannery industry in China could reach up to 10.7 [177], which is within the working conditions range of the hydrogels investigated in this study. The adsorption capacity of starch-graft-itaconic acid hydrogels for Cr(III) may be ascribed to their functional groups, such as R-CO-R' and R-COOH, and their electrostatic attraction with the aqueous forms of Cr(III). This assertion is corroborated by Bandara et al. (2020) [178] and Olawale et al. (2022) [179], who state that electrostatic interactions involving functional groups that contain oxygen are crucial for the adsorption of Cr(III). Carbonyl groups of this type have also been shown to form complexes with metals through oxygen-donating electron pairs [94]. This is because aqueous forms of Cr(III) and Cr(VI) exist as complex ions rather than isolated ions.

The redox potential (Eh), the Cr concentration, and the presence of oxidizing and reducing agents all influence the aqueous forms of chromium [16]. The equilibrium between the aqueous forms of Cr is illustrated in the Pourbaix diagram of Cr-H<sub>2</sub>O (Figure 4.6). This diagram shows that Cr(VI) exists predominantly as chromic acid (H<sub>2</sub>CrO<sub>4</sub>) at pH values below 1.0. Then, for pH values between 2.0 and 6.0, hydrogen chromate ions (HCrO<sub>4</sub><sup>-</sup>) and dichromate ions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) are in equilibrium. At pH values over 6.0, chromate ions (CrO<sub>4</sub><sup>2-</sup>) are the main form of Cr(VI) in solution. As a result, Cr(VI) (oxyanions with a strong oxidizing capacity under acidic conditions) is generally in solution as negative ions and is thereby favorably adsorbed under acidic conditions to positively charged surfaces [180].



Figure 4.6. Pourbaix diagram of Cr-H<sub>2</sub>O at 25 °C. Concentration of total Cr = 10<sup>-6</sup> M. The area limited by the dotted lines represents the stability of water. Adapted from Markiewicz et al. (2015); Liu et al. (2016); Zhang and Tian (2020) [94,180,181].

Normally, as the pH is more acidic, the protonation of the adsorbent's functional groups increases; therefore, the uptake of Cr(VI) is more likely to occur. Under basic pH conditions, the predominance of OH<sup>-</sup> groups creates electrostatic repulsion forces among negatively charged Cr(VI) ions, which hampers their adsorption by the hydrogels [76]. Additionally, the size of the ions also has an effect on their adsorption by the hydrogels. For example, dichromate ions are larger than chromate ions, which generate a greater steric effect on the surface of hydrogels than smaller ions [182]. Regarding Cr(III), at pH levels below 4.0, Cr(H<sub>2</sub>O)<sub>3</sub><sup>3+</sup> is the main form of Cr(III) [94,180]. At pH values between 4.0 and 6.0, Cr(OH)<sup>2+</sup> and Cr(OH)<sub>2</sub><sup>+</sup> are the two primary

forms of Cr(III) in solution [180]. At pH values above 6.0, the most common aqueous forms of Cr(III) may include Cr(OH)<sup>2+</sup>, Cr(OH)<sub>4</sub>, and Cr(OH)<sub>3</sub><sup>0</sup> [180,181]. Therefore, Cr(III) is generally in solution as positively charged ions; as a result, it is typically adsorbed to negatively charged surfaces, such as those of starch-graft-itaconic acid hydrogels due to their functional groups. Furthermore, ion exchange between the Na<sup>+</sup> ions, as well as surface complexation with the hydrogels carboxyl groups may also be involved in the adsorption mechanism of Cr(III) [37,97]. Table 4.3 presents the comparison of the adsorption capacity of starch-graft-itaconic acid hydrogels for Cr(III) with other hydrogels reported in the literature. Despite the lower adsorption capacity of starch-graft-itaconic acid hydrogels, their synthesis is environmentally friendly. However, to improve the hydrogels' adsorption capacity for Cr(III) and the adsorption equilibrium time, one possible solution may be to increase the hydrogels surface area with an uniform pore size by using a spray drying procedure to make hydrogel microspheres [74].

Table 4.3. Adsorption capacity of starch-graft-itaconic acid hydrogels in comparison to other adsorbents in the literature for Cr(III) adsorption.

Hydrogel	Dry weight hydrogels/g	Initial concentration Cr(III)/(ppm)	Solution volume/ L	Contact time/h	Initial pH	qe/(mg /g)	Refere nce
Soybean dregs- poly(acrylic acid) hydrogels	0.03	100	0.035	0.5	6.0	~ 40	[105]
Graphene oxide/alginate hydrogel membrane	N/A	40	0.3	24	6.0	~ 50	[100]
Chitosan-sodium alginate hydrogels	0.15	700	0.05	1.5	5.0	~ 48	[98]
Carboxymethyl cellulose-g- poly(acrylic acid- co-acrylamide)	0.015	10	N/A	6	7.0	47.7	[97]
Starch-craft- itaconic acid hydrogels	0.1	100	0.05	24	8.0	14.13	This work

N/A: not available

# 4.4.4. Effect of Cr solution volume on the single-component adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels

Several volumes of Cr(III) and Cr(VI) solutions were tested to determine their effect on the adsorption by starch-graft-itaconic acid hydrogels (Figure 4.7). This may also be interpreted as a ratio of hydrogel mass per volume, such as 7 g/L (0.1 g/0.015 L), 3 g/L (0.1 g/0.035 L), and 2 g/L (0.1 g/0.05 L). The uptake of Cr(III) was 1.59 mg/g  $\pm$  0.15 mg/g (10.29 % wt removal) with 15 mL, 3.54 mg/g  $\pm$  0.36 mg/g (9.78 % wt removal) with 35 mL, and 2.91 mg/g  $\pm$  0.40 mg/g (5.64 % wt removal) with 50 mL. In contrast, Cr(VI) adsorption with 15 mL, 35 mL, and 50 mL was  $0.81 \text{ mg/g} \pm 0.24 \text{ mg/g}$  (5.66 % wt removal), 1.97 mg/g  $\pm 0.21 \text{ mg/g}$  (5.89 % wt removal), and 1.45  $mg/g \pm 0.75 mg/g$  (3.03 % wt removal), respectively. The adsorption of Cr(III) and Cr(VI) with 35 mL of aqueous Cr was the highest compared to the rest of the volumes. Regarding the adsorption of Cr(III), the statistical difference between the means of 15 mL, 35 mL, and 50 mL is significant (p-value = 0.015), but between 35 mL and 50 mL, the difference is insignificant (two-tail p test = 0.316), assuming equal variances. Similarly, the statistical difference between the means of 15 mL, 35 mL, and 50 mL in the uptake of Cr(VI) was insignificant (*p*-value = 0.295), and the difference was also insignificant between 35 mL and 50 mL (two-tail p test = 0.573), assuming unequal variances. Perhaps the higher ratio of hydrogels to volume of chromium solution hampers the adsorption of Cr(III) and Cr(VI) due to steric and electrostatic interactions between the Cr ions.



Figure 4.7. Effect of volume on the adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels. Error bars with 95 % confidence level from three replicates. The pH of the chromium solutions was not adjusted; the pH of Cr(III) was 3.1 and the pH of Cr(VI) was 4.5.

## 4.4.5. Binary adsorption of Cr(III) and Cr(VI)

The adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels was evaluated in binary-component systems with three different volume fractions: 30 % v/v Cr(III) (15 mL of Cr(III) with 35 mL of Cr(VI)), 50 % v/v Cr(III) (25 mL of Cr(III) with 25 mL of Cr(VI)), and 70 % v/v Cr(III) (35 mL of Cr(III) with 15 mL of Cr(VI)), as shown in Table 4.4 and in Figure 4.8. The overall Cr uptake of Cr(III) and Cr(VI) with 30 % v/v Cr(III), 50 % v/v Cr(III), and 70 % v/v Cr(III) was 0.33 mg/g  $\pm$  0.46 mg/g (0.72 % removal), -0.47 mg/g  $\pm$  0.93 mg/g (-1.04 %), and 0.85 mg/g  $\pm$  0.73 mg/g (1.83 %), respectively. There was an insignificant difference between the three volume fractions of the binary systems with Cr(III) and Cr(VI) (*p*-value = 0.479). However, compared to the single adsorption system with 35 mL of Cr(III), the binary system with 70 % v/v adsorbed almost 2.0 mg/g less Cr(III). Therefore, Cr(VI) had an antagonistic effect on the adsorption of Cr(III) by the hydrogels. Some attempts aimed at resolving this issue may include developing biobased hydrogels with the ability to remove specific metals synergistically, even in binary metal systems, with the inclusion of organisms such as immobilized enzymes, for example [152].

Table 4.4. Effect of chromium solution volume on the binary adsorption of Cr(III) and Cr(VI) by starch-graft-itaconic acid hydrogels.

Sample	Cr267/ ppm	Cr283/ ppm	Average (Cr267, Cr283)/ppm	Average (Cr267, Cr283 * DF 1:10)/ppm	Average of replicates/ppm	q <sub>e</sub> /(mg/g)	SD	95 % Confidence	Standard error	Average q <sub>e</sub> /(mg/g)	Removal efficiency
25 mL Cr(III) + 25 mL Cr(VI)-1	8.67	9.17	8.92	89.2	92.6	1.2	1.62	1.83	0.93	$\textbf{-0.47} \pm 0.93$	-1.04%
25 mL Cr(III) + 25 mL Cr(VI)-2	9.05	9.51	9.28	92.8		-0.6					
25 mL Cr(III) + 25 mL Cr(VI)-3	9.30	9.83	9.57	95.7		-2.0					
15 mL Cr(III) + 35 mL Cr(VI)-1	9.11	9.61	9.36	93.6	92.2	-0.4	0.80	0.90	0.46	$0.33\pm0.46$	0.72%
15 mL Cr(III) + 35 mL Cr(VI)-2	9.00	9.49	9.25	92.5		0.2					
15 mL Cr(III) + 35 mL Cr(VI)-3	8.78	9.31	9.05	90.5		1.2					
35 mL Cr(III) + 15 mL Cr(VI)-1	8.97	9.47	9.22	92.2	92.2	0.9	1.28	1.44	0.74	$0.85\pm0.73$	1.83%
35 mL Cr(III) + 15 mL Cr(VI)-2	8.71	9.22	8.97	89.7		2.1					
35 mL Cr(III) + 15 mL Cr(VI)-3	9.22	9.73	9.48	94.8		-0.4					

DF: dilution factor

SD: standard deviation





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## 4.5 Conclusions

The adsorption of Cr(III) and Cr(VI) by biobased starch-graft-itaconic acid hydrogels in single and binary component aqueous solutions was evaluated using batch adsorption experiments at room temperature with continuous mixing for 24 hours. Considering that the stable forms of Cr(III) and Cr(VI) are pH dependent (hence their electronegativity properties) and that the ionic state of the functional groups on the hydrogels is also pH dependent, the pH of the solution could be used to leverage the selective adsorption of Cr(III) and Cr(VI). This study found that the starch-graft-itaconic acid hydrogels were highly selective for Cr(III) over Cr(VI) with optimal adsorption capacity at pH 8.0. Heavy metal pollution poses a major risk to all living organisms due to its toxic effects and this research showed that starch-graft-itaconic acid hydrogels may be a suitable biobased material for removing Cr(III) from contaminated water. These hydrogels would ideally be used on a wide scale to treat some industries' effluents (e.g., the tannery industry), but additional research employing continuous flow adsorption would be needed.

## 5. General discussion and general conclusions

The general objective of this thesis was to evaluate starch-graft-itaconic acid hydrogels for the adsorption of Cr(III) and Cr(VI). According to the hypothesis, starch-graft-itaconic acid hydrogels may selectively adsorb heavy metals in function of their oxidation state. This chapter reflects on the research findings, their interpretation, implications, practical applications, and limitations, and ends with some future research suggestions.

Biobased hydrogels are often investigated in adsorption systems containing multiple heavy metals with the same oxidation state, such as Pb(II), Ni(II), Cu(II), and Zn(II). Therefore, the focus of this work was to study the adsorption behavior of heavy metals with more than one stable oxidation state, for example, Cr(III) and Cr(VI). In this work, it was found that the adsorption of Cr(III) and Cr(VI) by starch-graft itaconic acid hydrogels is significantly dependent on the pH of the solution. For example, at pH 8.0, the adsorption of Cr(III) reached 14.13 mg/g  $\pm$  0.42 mg/g. On the contrary, the adsorption of Cr(VI) was less than 1.5 mg/g from pH 2.0 to pH 10.0. The functional groups of starch-graft itaconic acid hydrogels, the ionic form of Cr, and the adsorption mechanism may have contributed to this behaviour. Oxygen-containing functional groups (e.g., hydroxyl, carboxyl) of starch-graft-itaconic acid hydrogels may have deprotonated and become negatively charged groups. Cr(III), on the contrary, was mainly stable as positively charged ions (e.g.,  $Cr(H_2O)_3^{3+}$ ,  $Cr(OH)^{2+}$ ,  $Cr(OH)_2^+$ ,  $Cr(OH)^{2+}$ ,  $Cr(OH)_4^-$ , and  $Cr(OH)_3$ ). Accordingly, this difference in the ionic charges between Cr(III) ions and the hydrogel surface charge may have led to a higher uptake of Cr(III) over Cr(VI) by the hydrogels due to electrostatic interactions, but because of the carboxyl functional groups of the hydrogels, ion exchange and surface complexation may have also been involved in the adsorption mechanism. These findings support the notion that the functional groups of hydrogels, containing oxygen, nitrogen, sulfur, and phosphate, have a significant impact on the adsorption process, and may influence their selectivity for certain oxidation states of aqueous heavy metals, which in this case were selective for Cr(III) over Cr(VI).

Furthermore, these findings added to the understanding of the adsorption behavior of Cr by biobased hydrogels in that biobased hydrogels may selectively remove aqueous heavy metals based on their oxidation states, and that their adsorption behavior may be broadly predicted by considering the physicochemical properties of the metals, biobased hydrogels, and aqueous system. The adsorption results of this work verified the notion that the ionic form of heavy metals may be unique for each of their oxidation states, as is the case with Cr. The heavy metal physicochemical properties such as the molecular size and electronegativity may also determine their adsorption behavior by biobased hydrogels. Metals with large ionic radii of metals causes stronger steric effects than metals of smaller size, limiting their absorption by hydrogels. Finally, the aqueous system conditions such as the presence of other ions (e.g., H<sup>+</sup>, and OH<sup>-</sup>), organic and inorganic matter may negatively impact the metal adsorption capacity of biobased hydrogels. Therefore, biobased hydrogels may have the potential to be used in water treatment facilities and industrial effluents for the selective removal of heavy metals.

In this study, the concentrations of Cr(III) and Cr(VI) were determined using ICP-OES, which only reports the total chromium content. Therefore, to improve the accuracy of the data for binary adsorption systems, it may be recommended that future research determines the precise quantity of Cr(III) and Cr(VI) using ion chromatography, for example. Additionally, functional groups containing nitrogen (e.g., amines, quaternary ammonium groups) could be grafted onto starch-graft-itaconic acid hydrogels to selectively target the adsorption of negatively charged metal ions, such as Cr(VI). Nonetheless, further research is necessary to understand the adsorption mechanism, which might be determined using X-ray photoelectron spectroscopy (XPS). Furthermore, the number of metal adsorption cycles that starch-graft-itaconic acid hydrogels can withstand may be useful to assess their life cycle. Finally, determining the kinetics and thermodynamics of Cr(III) adsorption by starch-graft-itaconic acid hydrogels may also be of interest.

Lastly, some considerations regarding the experimental section of this study are provided. A few remarks should be made about the synthesis of starch-graft-itaconic acid hydrogels. Because the synthesis process is temperature sensitive, an oil bath with a thermocouple connected to the hot plate is highly suggested. Furthermore, certain hydrogels may adhere to the petri dish during the oven drying process; in this instance, a porcelain crucible may be used instead to oven-dry the hydrogels. In terms of the adsorption experiments, it should be emphasized that, in addition to measuring the volumes, the mas was also measured in order to assure the smallest margin of error. Moreover, because the adjustment of pH increases the volume of the Cr solutions, the concentration of Cr in solution may decrease. As a result, it is advised that the metal solution be prepared at a concentration 5 % to 10 % higher than the intended concentration.

Furthermore, there is a lack of studies that illustrate the relationship between the hydrogel retention of the metal solution (swelling) and their respective adsorption capacity for heavy metals, depending on the pH of the solution. The water swelling capacity of the hydrogels at various pH values is commonly reported, followed by their metal adsorption capacity as a separate section. As a result, this study aimed to establish a relationship between the swelling capacity of hydrogels and their heavy metal adsorption ability. However, the evidence was inconclusive or there was no clear association. The hydrogels might have swelled greatly when in contact with the metal solution while only retaining negligible quantities of Cr, and vice versa. Given this, it is worth considering how important it is for hydrogels to have the highest swelling capacity at the pH where the highest metal adsorption also occurs. According to the literature, there are two major elements to consider: the system setting, and the three-dimensional structure of the hydrogel.

In the event of a batch system, a similar pH value for the maximum water-swelling ratio and metal adsorption would be desirable. In contrast, for a continuous flow system, it is preferable to have low swelling kinetics while assuring maximum metal adsorption. This is because, in a continuous adsorption column, the adsorbent should persist as long as feasible without needing to be replaced. This would be made possible by a decreased in their swelling dynamics. The last factor is the degree of crosslinking, which is the most important element influencing the swelling ratio of the hydrogel. For example, a larger swelling ratio is associated with a decreased crosslinking of the hydrogel. However, poor cross-linking has a negative influence on the structure of the hydrogel. Therefore, it would be ideal to establish a balance between these two.

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