Pectin-Based Material for Applications in Water Treatment

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Climate change and water are inseparably connected. Extreme weather events cause water to become more scarce, polluted, and erratic than ever. Pectin is a biodegradable polymer, extractable from vegetables, and contains several hydroxyl and carboxyl groups that can easily interact with the contaminant ions. In addition, pectin-based materials can be prepared in different forms (films, hydrogels, or beads) and cross-linked with several agents to change their molecular structure. Consequently, the pectin-based adsorbents can be tuned to remove diverse pollutants such as divalent metals.

Keywords: pectin ; low methoxylation degree ; adsorption ; cross-linking

1. Pectin—Chemical Structure

Pectin is an anionic heteropolysaccharide that is present in vegetable cell walls. Pectin is particularly predominant in fruit peels, especially in citrus peel and apple pomace, but also in passion fruit rind, pomelo, and banana peel ^[1]. The pectin backbone chain comprises α -(1,4)-linked D-galacturonic acid (GalA) residues ^[2] (mainly homogalacturonan (HG), rhamnogalacturonan I (RG-I), rhamnogalacturonan (RG-II)) linked by α 1-4 glycosidic bond. The homogalacturonan (HG) is the most abundant and linear domain (around 60%).

The carbon 6 of the D-galacturonic acid residues can be methyl-esterified (COOCH₃) or carboxylated (COO⁻, in its deprotonated form). It also can be acetylated at the O-2 and/or O-3 position of the GalA residues, although this is less common ^[2]. Depending on the ratio of the methyl-esterification of these residues, pectin shows a different esterification degree (DE).

Carboxyl groups are hydrophilic and can coordinate with metal ions, whereas methyl-esterified are phobic. Therefore, by maximizing the number of COO^- (i.e., low degree of esterification), the adsorption efficiency against metal ions is much higher than pectin with a high amount of $COOCH_3$ groups.

DE is a magnitude that is related to the gelling mechanism of pectin. It classifies pectin into two groups: high methoxyl pectins (HM), where more than 50% of the galacturonic acid residues are esterified, and low methoxyl (LM) pectins, where less than 50% of the galacturonic acid residues are methoxylated. Independent of the DE, pectin is a water-soluble biopolymer. Therefore, it should become insoluble to be used as an adsorbent in aqueous environments. This can be achieved by cross-linking the pectin with various cross-linking agents, as described in the next section.

Pectin sources (i.e., the plant used to extract pectin) strongly influence the galacturonic acid content and the degree of methoxylation obtained after extraction ^{[3][4]}. These two variables directly affect pectin's ability to form a gel. The most common sources of pectin are apple pomace and citrus peels. Whereas the galacturonic acid content for apple pomace is between 20 and 44%, and the orange peel has been higher in comparison.

There are different extraction methods to isolate pectin from vegetables, which also affect the structure of the pectin, and it involves several steps (pretreatment, extraction, purification, concentration, precipitation, drying, and standardization) ^[5]. The preferable method is to mix the cell-wall materials in hot or cold acidified water $^{[6][Z]}$ because the highest extraction yield is achieved. It is also possible to add chelating agents ^[8] such as cyclohexane-diamine-tetra acetic acid (CDTA), oxalate, or ethylene-diamine-tetra acetic acid (EDTA) to promote the release of pectin. On the other hand, if instead an acidic alkaline extraction is used, the length of the galacturonic acid, the methoxylation degree (DM), and acetylation (DA) decrease ^[9].

The possible uses of pectin in different industries are abundant and of different natures, mainly in the health and pharmacy sector, food applications, and packaging. As pectin is a natural component of vegetables and fruits, it is an

exceptionally safe multifunctional food additive (E440) that is used, for example, as a texturizer or gelling agent. In addition, pectin is popular in several scientific fields because of its availability, safety, relatively low price, and functionality. Specific structural attributes developed by pectin's functional groups or the attachment of chemicals on the molecule make it a good candidate for several purposes, such as food innovations ^[10], nutritional remediation ^[11], drug delivery ^[12], illness treatment ^[13], tissue engineering ^[14], and other approaches ^[15]. Notably, pectin is resistant to gastrointestinal hydrolyzing enzymes and acidic/alkaline media, which favors its application in colon delivery via an oral route under a specific condition.

In particular, pectin, with a low level of esterification, also has a high application value and broad application prospects as a functional food ingredient $^{[16]}$. It also has been studied as a forthcoming biomaterial for tissue engineering and biomedical applications $^{[17]}$. Pectin films have also been used in packaging, although there are some limitations because of their inadequate mechanical properties and high hydrophilicity of the pectin films $^{[18][19]}$. This issue can be solved by blending with other polymers $^{[20]}$ or incorporating cross-linkers and/or filler material $^{[21]}$.

2. Insoluble Pectin—Cross-Linking Agents That Generate Gelation

As mentioned above, pectin is a water-soluble material. Therefore, it must be insolubilized to be used as an adsorbent to remove pollutants from water. Different ionic crosslinking agents were used for pectin The cations monovalent (Na⁺, K⁺), divalent (Ca²⁺, Cu²⁺, Sr²⁺ Ni²⁺ Zn²⁺ Cd²⁺ Pb²⁺ or Mg²⁺), or trivalent (Al³⁺, La³⁺, and Fe³⁺) are the most used. Pectin can also be cross-linked using non-ionic cross-linkers such as glutaraldehyde ^[22] or laccase ^[23]. However, ionic crosslinking is the most widely used and suitable method because it has the principal advantage of releasing contaminants (in some cases, recovering a priceless pollutant) and recovering the absorbent that can be reused.

Among all the possible ions, the divalent cations are the most commonly used elements for LM pectin gelation. After cross-linking (independent of the cross-linking agent), pectin undergoes gelation, producing a three-dimensional network in the form of xerogels (vacuum drying), hydrogels (wet gels), aerogels (supercritical CO_2 drying), and cryo-gels (freeze-drying) depending on the drying conditions ^[24]. The primary characteristic of wet gels is their ability to bind considerable quantities of water, thus increasing their volume. In addition, the swelling favors the access of pollutants to pectin.

The gelation mechanism of pectin is mainly governed by the methyl-esterification degree. Therefore, the gel formation mechanism differs for high-methoxyl (HM) and low-methoxyl (LM) pectins ^[25]. Apart from the methyl-esterification degree, the gelling process is influenced by ionic strength, molecular weight, and pH ^[26]. In addition, after cross-linking, the final structure of pectin depends on the cross-linking cation used.

There are fewer reports on LM pectin cross-linking using monovalent cations such as sodium (Na⁺) and potassium (K⁺). Cross-linking with these monovalent cations is produced at a low pH (approximately from pH = 2 to pH = 4) ^{[27][28][29][30]}. The cross-linking with monovalent ions diminishes the repulsive charges between pectin chains and promotes chain-chain association via hydrogen bonding ^{[27][30]}. It was suggested that at pH = 4.5, the cross-linking would more effective using K⁺ than Na⁺ because of the charge screening, galacturonic acid de-esterification, hydrogen bond changes, and electronic attraction ^[27]. Moreover, by increasing the pH to higher values (alkaline conditions), it was also found ^[22] that Na⁺ ions generated much stronger gels than those induced by K⁺ in HM pectin. In accordance, Yoo and coworkers ^[31] also studied poly (methyl esterase) mediated de-esterified citrus pectin when cross-linked with Na⁺, K⁺, and Li⁺. In agreement with Chen et al. ^[27], they observed that stronger cross-linking was produced using Na⁺ followed by K⁺ at pH = 7, whereas the reverse was true for pH = 5. A similar study was performed by Strom et al. ^{[30][31]}, where the influence of L⁺, Na⁺, and K⁺ on LM pectin rheology in an acid solution was evaluated. These investigations revealed that K⁺ formed the strongest gels, followed by Na⁺ and Li⁺. Furthermore, LM pectin was cross-linked by NaCI (0.05M) with and without ZnCl₂ ^[29] and could form nanoparticles. Li⁺ does not form gels at any of the tested conditions. This behavior was ascribed to an increase in the ionic radius of the hydrated cation.

Trivalent cations have also been employed as cross-linking agents for pectin [32][33][34][35]. It was found [32][33] that independent of the methyl-esterification degree, AI^{3+} binds pectin chains had the condition of $pH \ge 4$. In a rheological investigation [33], Ca^{2+} , Cu^{2+} , AI^{3+} , and La^{3+} ions were used as cross-linking agents. All these cations can form pectin gels. It was stated that the weakest gel was formed with La^{3+} , followed by Ca^{2+} , similar to AI^{3+} , while Cu^{2+} was one order of magnitude more substantial than the other cations. Finally, it was reported that the trivalent cations Fe^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} could establish cross-links in pectin [35]. In that work, the formation of isolated rhamnogalacturonan II dimers was reported. Still, there were no reports regarding what type of structure the pectin chains formed in the presence of these trivalent metals.

Apart from monovalent or trivalent cations, divalent cations such as Ca^{2+} are the most used cross-linking agents for pectin. The gelation of LM pectin with calcium ions occurs by forming junction zones according to the so-called "egg-box" model, which has been initially described for alginates ^[36]. The lower the pectin esterification degree, the more divalent the cation binding sites that are available on pectin, and the ability to absorb divalent cations increases. The following section will discuss the egg-box model from a historical perspective.

Many works have proven the effective cross-linking of LM pectin using Ca^{2+} [37][38][39][40][41][42][43][44][45]. In addition to Ca^{2+} , the cross-linking of LM pectin with Cd^{2+} and Cu^{2+} was reported for drug delivery applications [46]; Pectin was also cross-linked with Sr^{2+} and Zn^{2+} to form aerogels for diclofenac sodium controlled release [47]. Pectin cross-linked by Cu^{2+} ions was reported to be used as a scaffold for gold nanoparticles [48]. Moreover, pectin was cross-linked with a 2% (*w*/*v*) ZnCl₂ solution [49] to evaluate the potential healthcare applicability, and Das and coworkers [50] used LM pectin cross-linked with Zn^{2+} to encapsulate a colon-specific drug delivery microsphere.

On the other hand, other molecules have been used to induce the gelation of LM pectin. Yoshimura and coworkers ^[22] described the cross-linking of the LM pectin with ethylene glycol diglycidyl ether and glutaraldehyde or Ca²⁺. They found that glutaraldehyde produced pectin gels, whereas the ethylene glycol diglycidyl ether did not show an apparent gel formation. Ullah and coworkers ^[51] reported the cross-link of pectin with methylene bisacrylamide and ammonium persulfate as initiators. Pre-saponified pectin was also cross-linked with adipic acid ^[52] or adipic acid dihydrazide, which was previously involved in the oxidation of pectin ^[53]. Chen and coworkers compared the cross-link using adipic acid dihydrazide and the classic Ca²⁺ cross-link, reporting that the adipic acid dihydrazide cross-link significantly improved cell adhesion. Another example of a non-ionic gelling agent is laccase, which was employed to cross-link sugar beet pectin, as performed by Jung and Wicker ^[54], where they noticed an increase in the molecular weight of pectin by chromatographic techniques.

3. Structural Models of Cross-Linked LM Pectin and Alginates

3.1. Historical Perspective of Structural Models Induced by Calcium

In 1973, Grant and coworkers ^[36] first proposed the interaction between a polysaccharide chain (such as alginate or pectin) and divalent cations in terms of the egg-box model. Initially, this model introduced alginates: a non-branched polysaccharide composed of two monosaccharides, α –L guluronic and β -D mannuronic acids ^[55]. Using circular dichroism, the authors suggested a cooperative inter-chain mechanism of ion binding involving two chains associated with the coulomb interaction between the active sites and the metal ion. More specifically, two opposite α -L-guluronate sequences paired together to form a structure with cavities, within which Ca²⁺ ions were accommodated through specific coordination interactions between two free carboxyl groups.

Five years later, Morris et al. ^[56] studied alginate chain gelation by X-ray diffraction coupled with circular dichroism using different calcium concentrations. Their results showed that the primary inter-chain association mechanism was regularly dimerizing alginate or poly (guluronate) chain segments. This structure results in cross-linked dimers with a geometric design that resembles an egg box. Compared with the first proposal of the "egg-box" model, the dimers can further aggregate laterally into multimers, as revealed by small-angle X-ray scattering. In addition, the sugar ring belonging to guluronic acid and the polymer chain adopts a characteristic zigzag shape. Studying the lateral aggregation of dimers is essential to understanding the properties of these biomaterials in terms of their structure to explain what happens during a water remediation process. On the other hand, knowing the correct features and operating principle of the "egg-box" model helps to understand the possible pollutants of adsorption models from wastewater.

In 1981, Walkinshaw and Arnott ^[57] added, for the first time, the concept of the junction zone for the "egg-box" model for poly(galacturonic) acid and a high methoxylation degree of calcium pectate (i.e., pectin cross-linked with metal ions). In this new model, for poly(galacturonic) acid, chain–chain interactions were stabilized by intermolecular hydrogen bonds formed between several adjacent D-galacturonic acid units and hydrophobic bonding between methyl esters. Similarly, hydrophobic binding from segments of methyl groups and specific intermolecular hydrogen bonds stabilized calcium pectate. The main interactions between pairs of chains could be the bridges formed by calcium ions, which incorporate into their coordination shells two-polyanion oxygen atoms from one chain and three from the other. In addition, in 1982, Powell et al. ^[58] investigated rhamnose distribution for the formation of stable poly(galacturonic) acid inter-chain junctions for high and low degrees of methyl(esterification). Their results confirm the Walkinshaw and Arnott hypothesis ^[57]. They also indicate that the length of the poly(galacturonic) acid sequences between rhamnose interruptions (i.e., hairy regions) is approximately constant (i.e., they prove the existence of the junction zone).

Later, Kohn ^[59] studied the interaction between carboxyl groups and divalent cations in pectin fragments, resulting in a complex formation. The interaction exhibits different affinities towards divalent cations: Ca^{2+} , Sr^{2+} , and Zn^{2+} ions are bound according to the well-known "egg-box" model, whereas Cd^{2+} , Cu^{2+} , and Pb^{2+} form intra- and inter-molecular complexes.

At this point, and to bring all the above studies together, a book entitled the chemistry and technology of pectin ^[60] was first published in 1991. This event changed scientists' attitudes toward pectin research because of the exponential growth of publications in the following years.

During the first ten years of the 2000s, scientists began to study the "egg-box" model using various approaches, and different reconsiderations of the model have been proposed. A molecular simulation study ^[61], made on pairs of galacturonate oligomers, found a shift along the chain axis in the association of associated galacturonate chains. Therefore, they proposed the "shifted egg-box" model to explain the gelation mechanism of galacturonate chains, where two shifted antiparallel pectin chains are necessary to form the egg-box dimer.

In 2007, the "shifted egg-box" model for Ca-alginate gels was re-examined $^{[62]}$ and confirmed using X-ray diffraction measurements. Unlike previous "egg-box" models developed for pectin, in this case, the authors considered the helical conformation of the main chain, which had not been considered before. These results suggest that instead of a 2/1 helical conformation, as previously proposed for the egg-box model $^{[63]}$, a 3/1 helical conformation for the junction zones was energetically more favorable for these materials. In the same year, Fang et al. $^{[64]}$ studied the Ca²⁺-alginate gel of high (long polymer chain) and low molecular weight (short polymer chain) using isothermal titration calorimetry. They proposed a three-step binding behavior of calcium to alginate to form "egg-box" dimers: (i) the interaction of Ca²⁺ with a single guluronate unit forming mono-complexes (i.e., a carboxylic group with Ca²⁺); (ii) the propagation and formation of egg-box dimers via the pairing of these mono-complexes; and (iii) the lateral association of the egg-box dimers, generating multimers. The short chains are quite rigid, and inter-cluster association is the only possible way for the "egg-box" dimers to aggregate laterally. This aggregation increases in molecular size. However, long chains are more flexible and have smaller clusters. The intra-cluster association, in this case, results in a reduction in molecular size.

In 2008, Fang and coworkers [65] compared pectin with alginate for calcium-binding behavior. LM pectin is similar to alginate, but a two-step mechanism is involved. Whereas step I can be attributed to a mono-complex between Ca²⁺ ions and a polygalacturonate chain, step II is the formation of egg-box dimers through the pairing of the mono-complexes. In addition to steps I and II, the binding of alginate with Ca²⁺ includes a third step that is assigned to the lateral association of egg-box dimers.

In 2010, Gohil ^[66] studied the structural reorganization of pectin and alginate films after calcium binding by X-Ray diffraction and dynamic mechanical measurements. His results suggest that the structural reorganization of molecular network structure, after binding with Ca²⁺, destroyed some existing pectin crystalline tie points, resulting in its amorphization, as described by the "fringe-micellar" structure. In the same year, Fraeye and coworkers ^[41] summarized in detail how the characteristics of the final pectin gel are affected by different "intrinsic" and "extrinsic" parameters such as the amount and distribution of methyl ester, chain length, pectin concentration, amidation, and acetylation degrees, molecular weight, calcium content, temperature, and pH.

Ventura and coworkers $[\underline{67}]$ published a SAXS analysis of Ca²⁺–LM pectin gels with different calcium concentrations, coupled with molecular dynamics simulation studies. They proposed a new "egg-box" model considering semi-flexible and no linear chains. This chain flexibility was not considered in any of the previous models developed. They showed $[\underline{67}]$ that rod-like and point-like cross-links between neighboring pectin molecules could occur. With the increased Ca²⁺ concentration, the number of road-like cross-links decreased while the number of point-like cross-links increased.

Wang et al. ^[68] studied the high and low methoxyl pectin self-assembly molecules, which were regulated by calcium ions using atomic force microscopy (AFM) in the following years. The addition of calcium ions increased the viscosity of the low-methoxyl pectin solution. Otherwise, the viscosity of the high-methoxyl pectin solution remained stable. AFM confirmed that the esterification degree and calcium concentration cause different binding methods with calcium ions between pectin governed by the branched nature of pectin ^[67]. The formation of dimers by lateral aggregation was observed only for the LM-pectin. However, for the HM-pectin, the large number of esterified galacturonic acid residues limits pectin fiber aggregation due to the nonspecific hydrophobic interaction and hydrogen bonds.

3.2. Recent Evolution of Structural Models for Pectin Is Cross-Linked with Other Metals

As mentioned above, pectin is susceptible to cross-links with other cations apart from calcium. Specifically, in 2015, Assifaoui et al. ^[69] published the structural differences found in LM pectin when cross-linked with Ca^{2+} and Zn^{2+} . These results show that Ca^{2+} cations only interact with carboxyl groups and form more homogeneous pectin network fibers (i.e., the well-known "egg-box" dimers). In contrast, Zn^{2+} also interacts with hydroxyl groups, resulting in a less homogeneous cross-linked pectin network.

In 2016, Huynh et al. ^[70] investigated the binding mechanism using different cationic metals (Zn²⁺, Ca²⁺, Ba²⁺, Mg²⁺) by isothermal titration calorimetry, viscosity measurements, and molecular dynamics simulations in poly (galacturonic) acid. In this framework, a monodentate interaction meant the interaction between a carboxyl group of galacturonic acid and a cation. In contrast, a bidentate interaction means the binding of two oxygen atoms of the galacturonic acid (from two different pectin chains) and a cation. They reported that the interaction between divalent cations and poly (galacturonic) acid is monodentate for Mg^{2+} and Zn^{2+} and bidentate for Ba^{2+} and Ca^{2+} . Moreover, the binding mechanism for the divalent cations, Zn2+, Ca2+, and Ba2+, can be associated with mono-complexation and point-like cross-links or related to the appearance of the dimmers formation, depending on the molar ratio between the divalent cation and galacturonic acid $(R = Meta|^{2+}/Gal)$. This conclusion was based on the number of water molecules coordinated with the different cations. In the case of Zn^{2+} , Ca^{2+} , and Ba^{2+} , the coordination with water was weaker in strength than those of Mq^{2+} . During the cross-link, the metal ions lose one water molecule for the Zn²⁺ and two for Ca²⁺ and Ba²⁺, respectively. However, Mg²⁺ strongly interacts with water and remains weakly bound to poly(galacturonic) acid by sharing water molecules from its coordination shell with the carboxylate groups. Finally, two years later, Huynh et al. [71] studied the gelation kinetics of pectin induced from divalent cations (Zn²⁺, Ca²⁺, Ba²⁺, Mg²⁺) by viscoelastic and turbidity measurements. Their results confirmed that the cations' diffusion kinetics was lower for Zn^{2+} than for Ca^{2+} and Ba^{2+} . However, for the Mg²⁺, the gel was not formed, supporting a previous study [70].

4. Properties of Pectin That Influence the Absorption of Metal lons

Cataldo et al. ^[72] prepared pectate and poly(galacturonate) calcium gel beads for mercury (II) removal. Based on a different pH value study, they found that the best pH range for Hg^{2+} removal was between 3 and 3.6. Celus et al. ^[73] studied the ability of citrus pectin to adsorb Fe^{2+} , emphasizing two structural properties: the degree of methyl esterification (DM) and the degree of blockiness (ratio of non-methyl esterified GalA units present in blocks to the total amount of GalA units) of citrus pectin. They found that the DM and DBabs influenced pectin- Fe^{2+} interactions: the higher the DBabs or lower DM, the higher the Fe^{2+} binding capacity.

In another study, pectin micro-gel particles were also used to remove methylene blue (MB) ^[74]. The authors found very high absorption ratios, even with time shorter than 20 min. Additionally, LM pectin was used to clean mineral soils polluted with Cu^{2+} ^[75]. Recently, a sweet potato residue modified by high hydrostatic pressure (HHP)-assisted pectinase was prepared ^[76]. This material was used for Pb²⁺ removal. They showed that the modified sweet potato pectin exhibited more excellent adsorption performances for Pb²⁺ and Cu²⁺ than natural pectin.

LM Pectin was also mixed with other biopolymers, such as chitosan, to prepare chitosan-pectin gel beads, which were synthesized via a green method ^[77] to remove a collection of heavy metals (Cu²⁺, Cd²⁺, Hg²⁺, and Pb²⁺). They analyzed different variables such as the effect of pH, contact time, heavy metals concentration, temperature, and adsorption mechanism. They found that adding pectin increased the adsorption capacities, porosity, and stability of the adsorbents. The infrared analysis of the adsorbents indicates that the interaction between heavy metals and chitosan-pectin gel beads is due to the complexation with functional groups such as carboxyl, hydroxyl, amine, and amide.

Mata et al. $\frac{[78]}{2}$ prepared sugar-beet pectin xerogels using residues of the sugar industry. Their study is in conditions of continuous biosorption and not on stationary conditions as the above presented. In this case, the adsorbent was used for metal recovery from effluents in continuous systems. They studied different experimental conditions: feed flow rate and bed height (amount of biosorbent) and found that the best conditions for Cu²⁺ sorption in column reactors were: 3 g of biomass, 25 mg/L metal, 2 mL/min feed flow rate, and a reverse feeding system.

It is necessary to remark that there was a substantial dispersion of results obtained in the literature in relation to the adsorption capacity of pectin-based adsorbents. This is because the adsorption capacity of pectin strongly depended on its chemical characteristics and relied on both the source on which pectin was obtained and the extraction method. For instance, an early work by Kartel et al. ^[79] showed that apple pectin had the highest affinity for Co^{2+} ions, whereas, in the case of beet pectin, the affinity was better for Cu^{2+} and Cd^{2+} ions. In contrast, citrus pectin showed a different preference

for Ni²⁺, Zn²⁺, and Pb²⁺ ions. These different affinities depend on the structural differences of pectin. For instance, the galacturonic acid content for apple pomace is between 20 and 44% ^[80], whereas, for orange peel, it has been between 66 and 70% on a dried basis. In addition, apple pectin obtained from the different extraction procedures was highly methylated (from 54.5% to 79.5%) ^[9], but the methoxylation degree was much lower for orange peels. Thus, the source of pectin and the way it is extracted determines the structural properties of pectin, which, in turn, defines the adsorption capacity of heavy metals.

Among the different structural properties of pectin, the more critical parameter related to heavy metals binding is the methoxylation degree (DM) ^{[2][81]}. When DM is small, more carboxyl groups are available on pectin, which can interact with the metal ion, increasing the adsorption capacity. In addition, it has been reported that the pattern of methyl esterification is also crucial for determining adsorption capacities ^[82].

The influence of DM on the adsorption of metal ions has been studied for the adsorption of Zn^{2+} [83], Fe^{3+} [73], Ca^{2+} , Zn^{2+} , Fe^{2+} , and Mg^{2+} [84]. The influence on other structural parameters of pectin, such as the degree of acetylation (DA), chain length, or the branched domains, have been less studied concerning the adsorption capacity.

The molecular weight of pectin also influenced the adsorption capacity. The lower the molecular weight, the higher the adsorption capacity ^[85]. This effect occurs because small pectin chains can reveal additional active sites that can result in a more significant electrostatic attraction to capture more heavy metal ions ^[86]. In addition, a longer pectin chain can form a firmer gel in which the metal ions cannot penetrate.

In addition, due to the high degree of heterogeneity regarding chemical composition and physicochemical properties such as molecular weight, the degree of esterification, dispersion, and galacturonic acid content of the pectin, predictions of the metal-binding capacity of different pectin batches are quite tricky.

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