# Quartz Crystal Microbalance with Dissipation (QCM-D) as a Way to Study Adsorption and Adsorbed Layer Characteristics of Hemicelluloses and Other Macromolecules on Thin Cellulose Films: A Review

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Cellulose and hemicellulose are abundant renewable resources. Thus, studying the adsorption mechanism of hemicellulose adsorption onto cellulose will contribute to further understanding of the fiber network, promote the development of new materials, and improve the utilization rate of resources. Quartz crystal microbalance with dissipative (QCM-D) is a research tool that can monitor quality changes at nanograms level; it is often used in the field of adsorption. Starting from the interaction between cellulose and hemicellulose, this paper outlines research on the principle, influencing factors, and kinetics of hemicellulose adsorption onto cellulose by QCM-D and expounds the research methods and means in the field of adsorption of similar biomass that can be used for reference. It provides a reference for further study of adsorption mechanism.

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## INTRODUCTION

With the rapid development of the global economy, fossil resources, as the pillar of human social progress, are going to be exhausted. In order to solve this problem, the development of renewable resources with low energy consumption and small pollution has become a trend. Accordingly, biomass resources such as cellulose have become popular research objects (Mankar *et al*. 2021; Deng *et al*. 2022; Feng *et al*. 2022). As one of the most abundant renewable resources, cellulose is widely used in papermaking (Boufi *et al*. 2016), food (Kocira *et al*. 2021), medicine (Liu *et al*. 2022), environmental protection (Dong *et al*. 2021), and other fields. Hemicellulose, which is second only to cellulose in plant resources, tends to have a lower utilization rate during processing (Yao *et al*. 2017; Rao *et al*. 2019). Hemicellulose has lower polymerization degree and higher branching degree than cellulose. It is biosynthesized from different five- and six-carbon polysaccharide units and is often used as a source of value-added chemicals (Luo *et al*. 2019; Luo *et al*. 2021). The solubility of hemicellulose in water is not high. Hemicellulose mainly forms colloidal suspensions in solution, rather than becoming truly dissolved (Hubbe and Rojas 2008). In natural plant cells, hemicellulose plays an important biological role in connecting cellulose and lignin (Scheller and Ulvskov 2010). Exploring the interaction between cellulose and hemicellulose has played an important role in studying fiber structure and developing new polysaccharide materials (Mazeau and Charlier 2012). It has been found that the hydrophilicity and thermoelectric behavior of hemicellulose can be changed after chemical modification (etherification, esterification, oxidation, or polymerization) (Farhat *et al*. 2017; Yang *et al*. 2020). By such modifications, the performance and strength of the membrane formed by the mixing of hemicellulose and cellulose have been greatly improved (Li and Pan 2018). Hemicellulose is also often used as enhancer, adhesive, or an additive in pulp and papermaking (Bosmans *et al*. 2014; Zeng *et al*. 2022). It can also be used as an additive to increase the strength of paper (Lindqvist *et al*. 2013; Lee *et al*. 2015). Therefore, it is important to reveal the interaction between cellulose and hemicellulose.

The interaction between cellulose and hemicellulose in the course of manufacturing usually involves adsorption (Naidjonoka *et al*. 2020); however, it has been difficult to obtain the change of adsorption capacity of hemicellulose in real time and accurately during research. Fortunately, the method of quartz crystal microbalances with dissipative (QCM-D) can be used. QCM-D has an ultra-high mass resolution that can monitor small changes of surface mass with a precision in the nanograms range. Compared with other types of QCM measurements, QCM-D introduces the concept of a dissipative factor *D*, which can characterize the viscoelasticity of the layer on the surface of the sensor (Easley *et al*. 2022). QCM-D can be used with transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray diffractometer and other instruments to obtain more surface adsorption information.

## INTERACTION BETWEEN CELLULOSE AND HEMICELLULOSE

### Principle of Adsorption Between Cellulose and Hemicellulose

In natural wood, the cell wall of the plant consists mainly of cellulose, hemicellulose, and lignin (Gibson 2012). While the cell wall is being formed, hemicellulose completes its synthesis and deposition onto the cellulose, resulting in the interaction between the two (Rongpipi *et al*. 2019). Hemicellulose forms a dense network of fibers on the surface of the cellulose crystalline regions, which is connected by hydrogen bonds in the crystalline regions and van der Waals forces between molecules, and the strength between the fiber networks depends on the number of hydrogen bonds (Scheller and Ulvskov 2010). It is because of this physical crosslinking action that the space between crystalline microfibers and hemicellulose is flexible (Jin *et al*. 2019).

### Factors Affecting Hemicellulose Adsorption onto Cellulose

There are many factors affecting hemicellulose adsorption onto cellulose. For instance, it appears that the anionically charged nature and self-repulsion among typical hemicellulose macromolecular chains cause a three-dimensional, bulky adsorbed conformation of hemicelluloses, which leads to such properties.

Studies have shown that the factors affecting hemicellulose adsorption are related to the side chain structure and molecular weight of hemicellulose molecules. Linder *et al.* (2003) found that xylan is the diffusion effect and aggregation effect of xylan before adsorption on cellulose. Reducing the side chain of xylan by 4-O-methylglucuronic acid can increase the aggregation effect and thus increase the adsorption capacity of xylan.

Khodayari *et al*. (2021) studied the binding energy of glucomannan and xylan with different side chains to the hydrophilic surface of cellulose, finding that the O-acetyl group weakened the interaction between the two, whereas arabinose enhanced the interaction. It was also found that water can fill the gap between the two and form hydrogen bonds, weakening the adsorption interactions between the two. Wang *et al.* (2017) found that mannan with fewer side chains and lower molecular weight adsorbed more onto cellulose. Yao *et al.* (2021) extracted hemicellulose of different molecular weights by hydrothermal and alkaline extraction methods. The adsorption capacity of high molecular weight hemicellulose was high, the adsorption rate was faster, and the adsorption equilibrium was reached in a shorter time.

Similarly, the ion concentration of the solution system in which cellulose and hemicellulose are located also affects the adsorption. Tammelin *et al.* (2007) found that demethylation of hemicelluloses by hydrogen peroxide bleaching decreased their adsorption onto cellulose. They explained that the effect of ion concentration on adsorption is derived from the mutual electrostatic interaction of anions in hemicellulose molecules and the electrostatic repulsion of these anions and anions in the solution system, thus demonstrating that the adsorption is not merely electrostatically driven. Wang *et al.* (2016) found that by adding cations to the solution system, the electrostatic repulsion between the negatively charged hemicellulose and the negatively charged cellulose could be reduced, and the stability of the hemicellulose aggregate could be reduced, which promoted the sedimentation and adsorption of the hemicellulose. By contrast, when the side chain was not charged, arabinofuranose had little effect. Kohnke *et al.* (2009) used 2,3-epoxypropyltrimethylammonium chloride to cationicize xylan, which improved the surface affinity between the two and increased adsorption.

There have been few studies on the adsorption kinetic aspects of cellulose and hemicellulose, and the structure of hemicellulose is complex. It follows that there is no exact mechanism to explain the detailed dependencies of adsorption on specific factors, but there are still some studies on related aspects. Heinonen *et al.* (2022) studied the characteristics and preferential orientation of xylan adsorption on cellulose surface by molecular dynamics simulation. Khodayari *et al.* (2021) studied the surface morphology of cellulose adsorbed with different side chains of xylan by molecular dynamics simulation. Villares *et al.* (2015) used molecular dynamics to study concentrations and found that molecular rearrangement of xyloglucans in dilute levels after adsorption to the surface of cellulose nanocrystals (CNC), forming a flatter conformation, and xyloglucans at high concentrations were adsorbed to CNC, and the surface knots and forms more rings. Gu and Catchmark (2013) found xyloglucan in CNW (cellulose nanocrystalline whiskers) fits well with the Langmuir model. Dammak *et al.* (2015) and Pirich *et al.* (2015) studied the adsorption of different concentrations of xyloglucan on different fibers and found that isotherms fit the Langmuir and Freundlich models, respectively.

It should also be noted that different hemicelluloses have different solubility in water, and different concentrations of the same hemicellulose have different forms of dissolution in water, which is important for the study of adsorption. For example, tamarind xyloglucan forms self-assembled spherical nano-particles of 60 nm size at very low concentration, whereas hydrogels are formed at higher concentrations (Simi and Abraham 2010). Arabino-methylglucuronoxylan in softwood is partially soluble in water, while methylglucuronoxylan in hardwood is less soluble.

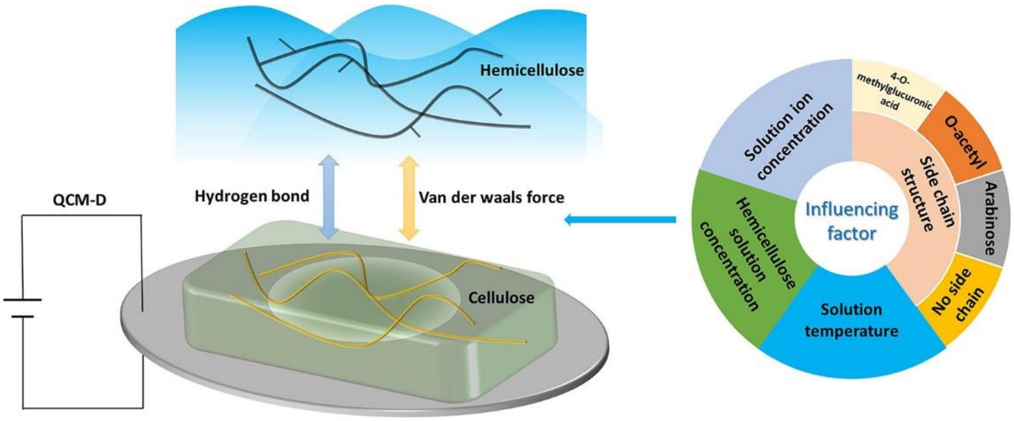

**Fig. 1.** Influencing factors of cellulose adsorption of hemicellulose

## Application of Cellulose Adsorbs Hemicellulose in Pulp and Papermaking Industry

In the pulp and paper making process, there will always be a small part of hemicellulose remaining on the surface of the fiber, mainly xylans and mannans. Moreover, much of the xylans and mannans that have been dissolved during the pulping process will be resorbed to the cellulose, which not only improves the fiber utilization rate and paper yield, but it also improves the performance of the paper. Dahlman *et al.* (2003) used softwood kraft pulp fibers to adsorb the xylans that was from black liquors, and after oxygen delignification and ECF bleaching, they were made into paper. As a consequence, the tensile strength and Z-strength (Scott Bond) of the paper has increased. Lee *et al.* (2015) use pretreatment to form polyelectrolyte layers on the surface of the cellulose, which improved the adsorption of xylan and increases the tensile and tearing properties of the paper. Kohnke and Gatenholm (2007) found that adsorption of 4-O-methylglucuronoxylan reduced the degree of crosslinking of drying-induced fiber walls and could be used as a hornification inhibitor, giving dried paper higher tensile strength and beatability. Schönberg *et al.* (2001) found that the location of xylans and the charge they carry have a large influence on the formation of bonds between fibers, thus affecting the strength properties of paper. For mannans, Hannuksela *et al.* (2002) studied how to increase the resorption of mannans to increase the yield of chemical pulp. In follow-up work, Hannuksela *et al*. (2004) used mannan to adsorption for modification of bleached kraft pulp (BKP) and thermomechanical pulp (TMP) respectively. They found that, compared with TMP, the effect on BKP was more obvious.

**Table 1.** Application of Hemicellulose as an Additive in Papermaking

| Additive Name | Function | | References |
|---|---|---|---|
| Xylan & Mannan | Increase paper yield | | (Hannuksela *et al*. 2002) |
| | Fiber utilization rate | | (Danielsson and Lindstrom 2005) |
| | Improve paper performance | Tensile strength | (Dahlam *et al*. 2003) |
| | | Tear properties | (Lee *et al*. 2014) |
| | | Beatability | (Kohnke and Gatenholm 2007) |

## Tools Commonly Used in Adsorption Research

The study of interactions is an essential part of many fields, for example, in the field of biomass, new materials can be developed, and utilization rate can be improved, *etc*. For this reason, it is particularly important to develop means of monitoring interactions, such as atomic force microscopy (Yao *et al*. 2021), dynamic light scattering (Arumughan *et al*. 2022), X-ray diffractometers (Wang *et al*. 2017), and contact angle measurement (Zhang *et al*. 2020). For cellulose and hemicellulose, the structure of the surface of the two is more complex, the difference in quality change during adsorption is very small, and most traditional detection tools can only detect the results after adsorption and cannot monitor the adsorption process in real time. QCM-D shows its unique ability to monitor its interaction processes in real time. QCM-D is a commonly used characterization tool for studying surface quality changes. It is used to determine the mass change at the nanogram level or the density change below 1 μg/cm$^2$. In a typical QCM-D test, the volume of the flow chamber can be as small as 0.05 cm$^2$, which means that it can be used for the determination of adsorption onto very small samples (Chen *et al*. 2016). Compared with other quartz crystal microbalance methods (QCM), QCM-D introduces the concept of dissipation factor D, so along with the dissipation measurement, the viscoelastic information of the film adsorbed on the sensor surface can be obtained (Fatisson *et al*. 2009).

**Table 2.** Tools Commonly Used in Adsorption Research

| Tools | Use stage | Purpose of use | References |
|---|---|---|---|
| Atomic Force Microscope(AFM) | After adsorption is completed | Observe the form of cellulose that adsorbed hemicellulose | (Yao *et al.* 2021) |
| High Performance Liquid Chromatography(HPLC) | Before and after adsorption completion | Compare the change of sugar content before and after adsorption | (Jaafar *et al*. 2019) |
| X-ray diffractometers(XRD) | After adsorption is completed | Measuring the crystallinity of cellulose | (Wang *et al.* 2017) |
| Contact angle measurement(CAM) | After adsorption is completed | Measure the change of film surface hydrophobicity | (Zhang *et al.* 2020) |
| Dynamic light scattering(DLS) | After adsorption is completed | Measure the particle size distribution of solution hydrodynamic diameter | (Arumughan *et al.* 2022) |
| Advantage | It can accurately obtain the changes of certain properties before and after adsorption | | |
| Challenge | Unable to monitor the change of adsorption process | | |

# INTRODUCTION TO QCM-D

## Principles, Mathematical Models, Adsorption Process Models of QCM-D

QCM-D is a measuring method based on the piezoelectric effect of quartz crystals (Su *et al*. 2018) . When the quartz crystal is deformed by external force, an electric field will be generated inside, and positive and negative charges will appear on its relative surface. QCM-D transforms the very small mass change on the crystal surface into a frequency change through this effect. The ratio of frequency and dissipation factor are then used to determine the viscoelastic information of the adsorption layer (see Table 2 for details).

**Table 3.** Fundamentals of QCM-D

| Name | Function | References |
|---|---|---|
| Sauerbrey formula | It is found that frequency (Δ*f*) is negatively correlated with mass (Δ*m*) | (Dickert and Latif 2017) |
| Dissipation factor D | Solve the problem of quality change of adsorption of viscoelastic adsorption layer | (Rodahl *et al*. 1995; Yao *et al*. 2021) |

In terms of adsorption kinetics, Adamczyk *et al*. (2022) have done a lot of summative work, such as planar substrate deposition kinetics and particle release kinetics in particle deposition kinetics. Chen *et al.* (2016) summarized the effects of different molecular forces (van der Waals force, electrostatic force, hydration force, *etc*.) on the adsorption characteristics of nanoparticles in classical and extended DLVO theory. The authors won't go into too much detail here.

## QCM-D *vs.* other QCM Methods

The most common QCM methods can only obtain the resonance frequency, and the energy loss has not been measured. As shown in Fig. 2b, QCM-R can measure *f* and resistance *R*. The output of *R* provides some information about viscoelasticity, but it cannot be quantified, so it is only suitable for thin and rigid films. QCM-D is suitable for all films, from thin to thick, as well as rigid and viscoelastic films.

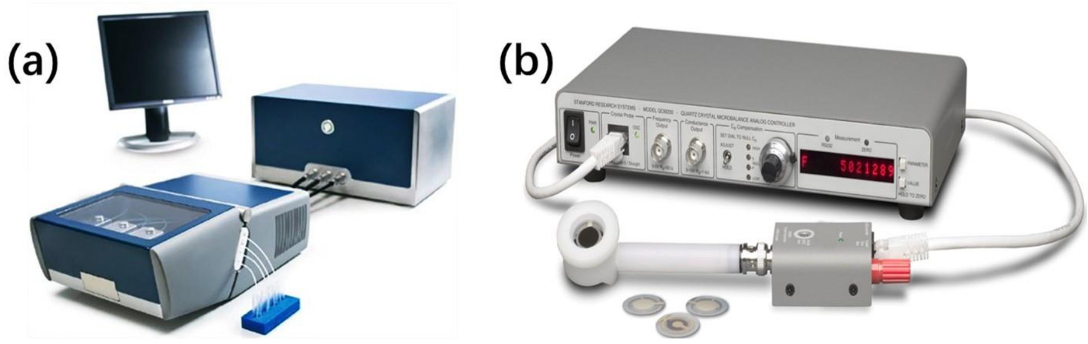

**Fig. 2.** QCM-D (a) and QCM-R (b)

## Reproducibility of QCM-D Measurements

The reliability and validity of test results depend on some assumptions and details related to the preparation of materials. Key aspects are as follows:

(a) The coating method of cellulose must be reproducible. This can be achieved by controlling the concentration of cellulose solution, the falling interval of each drop of solution, and the rotation acceleration and speed of the spin coater.

(b) The preparation of hemicellulose solution must be reproducible. Many scholars have proposed preparation methods, as cited in this article.

(c) The experiment of QCM-D must be reproducible. Fortunately, the flow rate and temperature of QCM-D can be accurately controlled.

### Application of QCM-D

QCM-D is widely used in the field of environmental governance. Gomez-Maldonado *et al.* (2019) decorated cellulose nanofibers (CNF) with β-cyclodextrin or poly(β-cyclodextrin) to remove cyanotoxins from water, and the adsorption behavior was monitored in real time using QCM-D. By such means, the maximum adsorption mass of decorated CNF for cyanotoxins was found to be 196 mg/g. Wang *et al.* (2022) studied the effects of $Ca^{2+}$ on bio-clogging of leachate collection systems in landfills, using QCM-D. They monitored the speed and viscoelasticity of bacterial attachment in the deposited layers. Combined with the DLVO theory, the $Ca^{2+}$ concentration was controlled at a low level. Such an approach can be used to reduce bio-clogging.

In terms of food applications, Dadmohammadi *et al.* (2022) used QCM-D to study the interaction between sweeteners and mucins to solve the problem of bitterness and astringency of sweeteners. Li *et al.* (2022) studied the emulsifying mechanism of persimmon pectin (PP), and used QCM-D to monitor the thickness, adsorption capacity and viscoelasticity of PP at the oil-water interface. They found that the multi-layer adsorption and high viscoelasticity of PP effectively blocked the flow of oil droplets and achieved better emulsifying ability.

In the field of medical health, Chen *et al.* (2022) studied the digestive resistance behavior of myofibrillar protein (MP)-soluble aggregates to gastric pepsin. They simulated the dynamic interaction of MP-soluble aggregates with gastric pepsin using QCM-D. The mechanism of effect of MP on intestinal digestion was further revealed. Sobiepanek and Kobiela (2022) used QCM-D to study glycans with different specificities on the primary tumor surface Interaction with specific lectins to reveal changes in cell viscoelasticity. Such an approach has potential for the development of specific, label-free biosensors.

## RESEARCH OF QCM-D IN SOME MICROPARTICLES ADSORPTION ONTO CELLULOSE

### Preparation of Cellulose Film

In the study of the behavior of macromolecules adsorption onto cellulose, it is difficult to measure untreated cellulose with QCM-D, so it is necessary to cover the sensor of QCM-D with a layer of film with good performance, uniformity, and stability. The common film preparation methods are the spin coating method (SC) (Villares *et al*. 2015; Jaafar *et al*. 2019; Yao *et al*. 2021) and the Langmuir-Blodgett method (Tammelin *et al*. 2007).

In the study of adsorption, spin coating is the most common method for preparing ultrathin films. The attributes of cellulose films prepared by spin coating will have a major effect on the dissipation measurements. Jaafar *et al.* (2019) used spin coating to prepare 9 nm ±5 nm CNC film, which was flat with dense layers. Eronen *et al.* (2011) used the same method to prepare flat and dense CNF film. The dense cellulose films will not affect the loose layers adsorbed next. It is also worth mentioning that films prepared with different substrates and different types of cellulose may also have an effect on the experiment. Different substrates will affect the degree of uniform distribution of cellulose films (Kontturi *et al.* 2007), and different types of cellulose will affect the degree of surface roughness (Amim *et al.* 2008). They may affect the surface area of cellulose films and then affect the adsorption.

**Table 4.** Coating Method of Cellulose

| Name | Frequency of Use | Basic Operation | Merit | Shortcoming | References |
|---|---|---|---|---|---|
| Spin coating method (SC) | Many | Anchor the cellulose film on the substrate with PEI solution (or other polyelectrolyte) | Simple operation and high repeatability | The film thickness can be controlled, but adjustment is difficult | (Villares *et al*. 2015; Jaafar *et al*. 2019; Yao *et al*. 2021) |
| Langmuir-Blodgett | Few | After film forming on the surface of organic solvent, compression and lifting are carried out with a vertically submerged solid substrate | Film thickness can be precisely controlled | Ion concentration and pH affect the performance of the film | (Tammelin *et al*. 2007) |

## Application of QCM-D for Microparticles Adsorption onto Modified Cellulose

The adsorption of polymers onto cellulose surfaces has attracted much attention on account of its applications in papermaking. The rapid development of layer-by-layer modification method on the surface of cellulose materials has further triggered a wave of research on the mechanism of polymers adsorption onto cellulose (Hammond 2011; Sun *et al*. 2022).

Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) is a conductive polymer (Malti *et al*. 2016; Ouyang 2013), which often used in conjunction with cellulose to develop conductive materials. Studies have shown that the two mainly interact through the formation of van der Waals force and a small amount of hydrogen bonds to complete the adsorption (Zhou and Hsieh 2018; Belaineh *et al*. 2019). On this basis, Jain *et al.* (2021) used QCM-D combined with atomic force microscopy (AFM) to study the adsorption of PEDOT: PSS on cellulose nanofibers (CNFs) and regenerated cellulose. In the experiment, temperature, pH, ion concentration and other factors as variables, monitoring adsorption process by QCM-D, and the morphology of the particles on the surface of the cellulose after adsorption was observed by AFM. The adsorption kinetics of PEDOT:PSS on the two cellulose was obtained. Adsorption of PEDOT:PSS was found to be a spontaneous reaction driven by entropy gain. Zhang *et al.* (2019) studied the adsorption behavior of amphoteric polyacrylamide (AmPAM) as a papermaking additive on microcrystalline cellulose (MCC) and use QCM-D to monitor the effect of different molecular weights of AmPAM on adsorption in real time. It was concluded that the optimal molecular weight range for increasing the dry strength of paper was between 300k and 500 k.

Carboxymethyl cellulose (CMC) is an anionic polyelectrolyte substance that has been shown to be functionalized by layer by layer adsorptive assembly onto cellulose (Liu *et al*. 2011; Wagberg and Erlandsson 2021). Arumughan *et al.* (2021) studied the effect of $Ca^{2+}$ and $Mg^{2+}$ on CMC adsorption by QCM-D. Compared with $Mg^{2+}$, $Ca^{2+}$ not only increased the adsorption mass of CMC, but it also made the adsorbed product more stable. On this basis, Aumughan *et al.*(2022) further studied the mechanism and driving force of $Ca^{2+}$ to promote adsorption. During QCM-D monitoring, the slope of the D–f curve decreased as the $Ca^{2+}$ concentration increased, indicating that the adsorbed CMC layer became denser. These findings were confirmed with dynamic light scattering (DLS) and electrophoretic mobility studies. It was concluded that CMCs promote adsorption in high concentration $Ca^{2+}$ solution mainly because the multichain association of CMCs increases the hydrodynamic diameter; The adsorption of CMC is driven by entropy, which is related to the release of water on the surface of cellulose.

## Application of QCM-D in Adsorption and Enzymatic Hydrolysis of Cellulose

In the hydrolysis of cellulose by cellulase, most researchers are engaged in two aspects of research. One is to study the adsorption behavior of some substances on the surface of cellulose and promote the hydrolysis efficiency of cellulase. The second is to study the adsorption behavior of different substances on the surface of lignin and study the effect of lignin on enzyme hydrolysis.

Lignin is connected to hemicellulose through lignin-carbohydrate complexes (LCC) in plant cells, and hemicellulose is linked to cellulose via hydrogen bonds and van der Waals forces (Sabiha-Hanim *et al*. 2015). The functional groups of amino acids in cellulase are mainly combined with lignin hydrogen bonds and electrostatic forces (Martin-Sampedro *et al*. 2013). For the adsorption by means of such small forces, QCM-D with ultra-sensitive monitoring capabilities has a unique advantage, and it can obtain subtle changes in the surface in real time.

Previous studies have discovered that bacterial expansin (BsEXLX1) can promote cellulase hydrolysis, but there are fewer studies on the adsorption behavior. Duan *et al.* (2018) used QCM-D to study the adsorption behavior of BsEXLX1 on the surface of cellulose. BsEXLX1 was introduced into the cellulose film prepared by the spin coating method. Then the frequency and dissipation changes in the process were monitored in real time. The molecular dynamics factors such as protein concentration of BsEXLX1 and the influence of surfactants on adsorption were studied, and the adsorption process was described by Langmuir model. BsEXLX1 was adsorbed with capacities up to 163.53 $ng/cm^2$. Zhang *et al.* (2021) based on Duan *et al.* further studied the adsorption behavior and hydrolysis process on the surface of cellulose of exoglucanases (Cel7A) and endoglucanases (Cel7B) in the presence of BsEXLX1. They found by tracking the adsorption in real time, at appropriate concentrations, that the initial adsorption rates of BsEXLX1-Cel7A and BsEXLX1-Cel7B were 2 times and 5.25 times that of Cel7A, respectively, and the final adsorption mass was 2.38 times and 2.69 times that of Cel7A. BsEXLX1- Cel7B exhibited a more obvious effect of catalytic degradation of cellulose.

In enzymatic hydrolysis experiments, pretreatment of residual lignin affects cellulase hydrolysis (Kumagai *et al*. 2016). Zhang *et al.* (2020) studied the adsorption of two cellulases, TvEG and TrCel7A, on the surface of lignin. The effects of the adding sulfonated lignin (SL) were evaluated. QCM-D was used to study the adsorption behavior of cellulase in real time, combined with dynamic light scattering (DLS), fluorescence intensity measurement, and ζ potential measurements to study the adsorbed lignin film. The adsorption capacity of TrCel7A for lignin was found to be higher than that of TvEG. After the addition of SL, SL and cellulase form a negatively charged complex, which prevents the adsorption of cellulase and lignin and promotes enzyme hydrolysis.

## APPLICATION OF QCM-D IN HEMICELLULOSE ADSORPTION ONTO CELLULOSE

Understanding the structure of hemicellulose, its interactions with cellulose, and its effects on cell wall structure and properties remains a key issue in the development and application of plant resources.

Some researchers (Khodayari *et al*. 2021) have used molecular dynamics simulations to study the interaction between cellulose and hemicellulose, but molecular dynamics simulations alone cannot handle overly complex adsorption systems. The advantage of using QCM-D is that it can accurately monitor the adsorption process and viscoelastic changes. Furthermore, it can be used to study the adsorption conformation and mechanism of hemicellulose with molecular dynamics simulation. Simply using molecular dynamics simulation can only predict the adsorption results. The adsorption between cellulose and hemicellulose is completed by van der Waals forces and hydrogen bonding. The time required to reach the saturation point of adsorption in the process is relatively long, and it is difficult to monitor because the adsorption mass is very small. Therefore, in recent years, many researchers have used QCM-D to study the adsorption between cellulose and hemicellulose.

### Preparation of Hemicellulose Solution

Preparation of hemicellulose solution is the starting point for studying adsorption. To begin, researchers usually obtain the required hemicellulose solid through such methods as alkaline treatment, hydrothermal treatment, steam extraction, and modification methods with a variety of woody materials (Naidjonoka *et al.* 2020). Next, researchers usually use water as the solvent of hemicellulose, and control the concentration of hemicellulose to be very low. Simi and Abraham (2010) found that when the concentration of xyloglucan is lower than 2000 μg/mL, 60 nm spherical nanoparticles will be formed. Chen *et al.* (2017) dissolved xylan in water with a concentration of 0.1 μg/mL and found that the size of hemicellulose particles was within 60 nm.

### The Mechanism of Hemicellulose Adsorption onto Cellulose

As already described, hemicellulose is deposited onto cellulose through the formation of hydrogen bonds and van der Waals force, which is similar to the form existing in natural wood. The related research, such as that listed in Table 5, found that hemicellulose solution concentration, solution ion concentration, solution temperature, and different side chain structure will affect the adsorption. This may be caused by the charge property of hemicellulose macromolecule itself. Therefore, scholars have further studied the adsorption process and adsorption conformation by using QCM-D, molecular dynamics simulations, and other instruments.

Many scholars have used QCM-D and other research instruments to study the molecular dynamics of adsorption, but due to the complexity and diversity of hemicellulose molecules and the large molecular weight distribution range, so far, no study has shown the main factors affecting the adsorption of hemicellulose.

Yao *et al.* (2021) used QCM-D to study the adsorption of arabino-4-O-methyl-glucuronoxylan of different molecular weights by alkaline and hydrothermal extraction methods on CNF. Adsorption kinetics was studied with QCM-D. When the concentration of hemicellulose was in the range of 50 mg/L to 300 mg/L, compared with pseudo-first-order and pseudo-second-order models, adsorption conformed to intraparticle diffusion kinetics (Fig. 3) (Yao *et al*. 2021). The cited authors therefore believe that adsorption can be divided into three stages: mass transfer, diffusion, and equilibrium. The thickness, viscosity and shear modulus of the adsorption film were analyzed by fitting the Voigt model. It was found that the adsorption rate of hemicellulose with high molecular weight was higher than that with low molecular weight, and the equilibrium time was shorter.

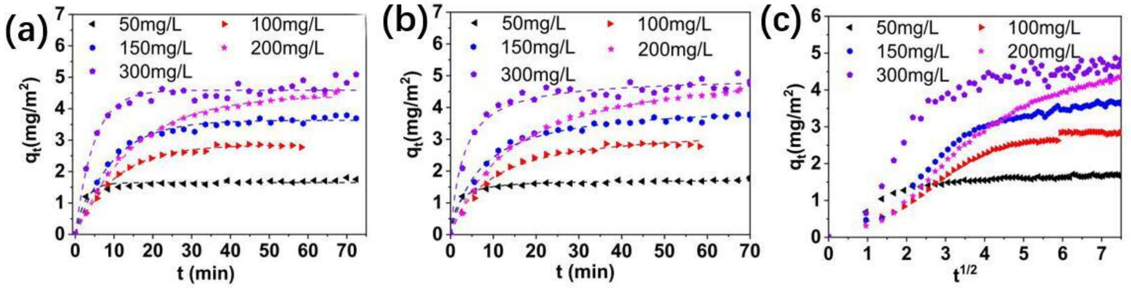

**Fig. 2.** Pseudo-first-order (a), pseudo-second-order (b), and intraparticle diffusion kinetic model (c); plots for hemicellulose adsorption on CNF at different concentrations. Figure republished from Yao *et al*. (2021) with permission from ACS.

**Table 5.** Kinetic Model of Hemicellulose Adsorption Process

| Cellulose | Hemicellulose | Hemicellulose concentration | Fitting phase | Model | References |
|---|---|---|---|---|---|
| CNC | Acetylated xylan<br>Deacetylated xylan | 0.3-20 μg/mL | Partial process before adsorption reaches saturation | Two-segment adsorption model | (Jaafar *et al*. 2019) |
| CNC | Xyloglucan | 0.01–20 μg/mL | | | (Villares *et al*. 2015) |
| CNC | Xyloglucan | 0.3-15 mg/L | | | (Villares *et al*. 2017) |
| CNF | Arabino-4-O-methylglucuronoxylan | 50-300 mg/L | The overall process after adsorption is completed | Intraparticle diffusion model | (Yao *et al.* 2021) |
| CNC | Xyloglucan | XG/CNC 25-250 μg/mg | | Langmuir model | (Dammak *et al*. 2015) |
| CNW | Xylan | 10-2000 μg/mL | | Langmuir model | (Gu and Catchmark 2013) |
| BCN (Bacterial Cellulose) | Xyloglucan | 200–500 μg/mL | | Freundlich model | (Pirich *et al*. 2015) |

Jaafar *et al.* (2019) studied the effect of acetylation on the adsorption of xylan. They used spin-coated CNC to adsorb acetylated xylan (XylAc) and deacetylated xylan (XyldAc) at different concentrations. They used QCM-D to monitor dissipation and frequency change, and the first and second kinetic constants of the adsorption process of XylAc and XyldAc at different concentrations were calculated, respectively. It was found that the adsorption of XyldAc is generally divided into two steps. Hemicellulose is rearranged on the surface of the cellulose to reach coverage. In the second step, hemicellulose is diffused by pre-adsorption to the layer of hemicellulose that has been adsorbed, forming a loose and more viscous layer. XylAc, due to the action of acetylation, has a better ability to cover cellulose than XyldAc, limiting the second step and forming a dense and hydrophobic rigid layer on the cellulose. Villares *et al.* (2015) studied the adsorption of xyloglucan on CNC using similar methods, and the authors argue that at low concentrations, the adsorbed XG molecules have time to rearrange. At high concentrations, XGs form more loops and tails on the surface of the CNC, the XGs will quickly cover the CNC surface to form an XG layer and prevent further rearrangement. Naidjonoka *et al.* (2020) compared the adsorption of galactoglucomannan (GGM) on the surface of hydrophobized silica and cellulose. They found that although GGM and cellulose are hydrophobic substances, there are some sugar groups, which make the adsorption capacity larger than that of hydrophobized silica.

Lee *et al.* (2014) used QCM-D to study the effects of different ion concentrations on the adsorption of cationic (quaternization) xylan (CX) with different amounts of charge. With consideration of Scheutjens-Fleer theory, the authors argue that the high ion concentration makes the cation preferentially combine with the anion sites on the low charge CX, thus reducing the adsorption. However, after the adsorption of CX with high charge, more coiled conformations will be formed, and the increase of ion concentration will promote the adsorption. On this basis, Lee *et al*. (2015) studied the effects of cationic polyelectrolytes with different charge amounts and molecular weights on xylan adsorption, and evaluated the viscoelasticity of the xylan layer by the Voigt model, concluding that the polyelectrolyte with high charge density made xylan adsorb faster at the beginning of adsorption, but the total adsorption mass was less than that of low-charge polyelectrolyte. High molecular weight polyelectrolytes make xylan molecules adsorb in the form of long loops and increases their thickness compared with low-charge polyelectrolytes.

## CONCLUSIONS AND PROSPECTS

In this paper, the application of quartz crystal microbalance with dissipation (QCM-D) in macromolecular adsorption is reviewed, and the adsorption of hemicellulose is emphasized. QCM-D has advantages in studying the adsorption process, but it still needs to cooperate with other methods and instruments to complete the experiment. QCM-D needs to maintain constant temperature during research. Any internal or external temperature change may cause the experiment to fail, so there may be some challenges in studying adsorption thermodynamics.

In the aspect of macromolecular adsorption, this paper introduces some new studies, hoping to provide research methods for hemicellulose adsorption for reference.

In the aspect of hemicellulose adsorption, adsorption kinetics is mainly based on the study of hemicellulose adsorption rate, process aspects, and influencing factors. In recent years, due to the real-time monitoring function of QCM-D, it has been used by many scholars to study the adsorption of different concentrations and different kinds of hemicellulose on different cellulose. Many studies have shown that due to the variety of cellulose and hemicellulose, changing the ratio of cellulose/hemicellulose concentration may change the kinetic model. Therefore, it is not clear which main factors affect the adsorption behavior, so the kinetics remains to be studied.

In terms of the influencing factor of ion concentration, although many people have used different ions for tests, few scholars have chosen different ions for horizontal comparison, for example, in the cellulose adsorption of CMC experiment, some scholars have done a comparative test on the effect of $Ca^{2+}$ and $Mg^{2+}$ on the adsorption. The corresponding experimental methods can still be used in the adsorption of hemicellulose.

Some scholars studied the effect of the adsorption position of xylan on the strength of the paper, and based on the technical means at that time, no further research was carried out on the adsorption mechanism. In the current research, most scholars focus on the orientation, surface conformation and process of hemicellulose adsorption, and there are fewer studies on the adsorption location, so the exploration of this mechanism still needs to be continued.

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