Adsorption Behavior of Cellulose and Its Derivatives toward Ag(I) in Aqueous Medium: An AFM, Spectroscopic, and DFT Study

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Supporting Information

ABSTRACT: The aim of this study was to develop a fundamental understanding of the adsorption behavior of metal ions on cellulose surfaces using experimental techniques supported by computational modeling, taking Ag(I) as an example. Force interactions among three types of cellulose microspheres (native cellulose and its derivatives with sulfate and phosphate groups) and the silica surface in AgNO₃ solution were studied with atomic force microscopy (AFM) using the colloidal probe technique. The adhesion force between phosphate cellulose microspheres (PCM) and the silica surface in the aqueous AgNO₃ medium increased significantly with increasing pH while the adhesion force slightly decreased for sulfate cellulose microspheres (SCM), and no clear adhesion force was observed for native cellulose microspheres (CM). The stronger adhesion enhancement for the PCM system is mainly attributed to the electrostatic attraction between Ag(I) and the negative silica surface. The observed force trends were in good agreement with the measured zeta potentials. The scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analyses confirmed the presence of silver on the surface of cellulose microspheres after adsorption. This study showed that PCM with a high content of phosphate groups exhibited a larger amount of adsorbed Ag(I) than CM and SCM and possible clustering of Ag(I) to nanoparticles. The presence of the phosphate group and a wavenumber shift of the P−OH vibration caused by the adsorption of silver ions on the phosphate groups were further confirmed with computational studies using density functional theory (DFT), which gives support to the above findings regarding the adsorption and clustering of Ag(I) on the cellulose surface decorated with phosphate groups as well as IR spectra.

INTRODUCTION

Atomic force microscopy (AFM) is a high-resolution technique with force measurement accuracy down to the piconewton level and has been regarded as a suitable tool for measuring the interaction forces since first being introduced by Ducker et al. Moreover, AFM was successfully applied to study the interaction forces between individual ligands and receptors under various conditions, such as the cellulose particle and silicon surface and alumina particle and sapphire surface in air and in aqueous media. In the past decade, cellulose microspheres with sizes of 15–30 μm have been successfully used as colloidal probes to study the interfacial interaction with AFM in aqueous solutions for the application of paper production. Most of these studies focused on interaction forces such as double-layer forces and osmotic forces between cellulose microspheres and ultrathin cellulose films upon addition of a series of cationic copolymers in aqueous electrolyte solution. However, none of these studies provided detailed investigations of the effect and adsorption of water contaminants on cellulose surfaces studied directly with the AFM technique.

Cellulose particles on micro- and nanoscales used as adsorbents for water purification have been an area of great interest in materials science research in recent years. Owing to the hierarchical structure and tailorable adsorption behavior via surface chemical modification with negative binding groups such as carboxylic, sulfate, and phosphate, cellulose has shown...
excellent potential to adsorb water pollutants such as dyes, pesticides, bacteria and virus, and a wide range of heavy metal ions including Ag(I), U(VI), Fe(III), Cu(II), Ni(II), Cr(III), and Zn(II). Our recent research activities on the use of nanocellulose and nanochitin for the adsorption of heavy metal ions, dyes, pesticides, and so forth from contaminated water have shown promising results. In spite of the positive results and the potential application of this technology in domestic and industrial water purification, mechanisms of adsorption and desorption of positively charged species on cellulose surfaces are largely unknown. Therefore, one or a combination of different techniques such as ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation, and microprecipitation are usually expected. Moreover, Volesky reported that sulfonate groups, carboxylic groups, and phosphate groups are all major metal-binding groups for biosorption.

Thus, the current study aims at a deeper fundamental understanding of the adsorption behavior and mechanisms of metal ions on cellulose microspheres in an aqueous medium, taking Ag(I) as an example. A large amount of Ag(I) is released into groundwater and surface water by many industrial operations such as the photographic and imaging industry as well as in electronics and electrical applications and cause serious health risks for humans exposed to these contaminants. Force interactions between cellulose microspheres with three types of surfaces (native cellulose and its derivatives with sulfate and phosphate groups) and a silica surface in an aqueous AgNO₃ medium at different pH values were measured to examine the effect of functional groups on the possible adsorption of silver ions. Measured adhesion and repulsion forces under various conditions provide valuable information about the extent of ion adsorption. The measured force curves on approach were analyzed using the DLVO (Derjaguin–Landau–Verwey–Overbeek) model to interpret the acting forces and to estimate the interaction parameters, such as the Debye length and the surface potentials.

Computational studies have been used as a complementary tool to gain more insight into the properties of cellulose and its surface interaction, inspired by some earlier studies found in the literature. For example, Li and co-workers investigated the structural and electronic properties of cellulose Iα and Iβ with DFT calculations. This group also studied cellulose interaction with water, and one of the conclusions was that the formation of hydrogen bonds between the cellulose and the water molecules depended strongly on the adsorption site. In another study by Bucko et al., the transition between cellulose Iα and cellulose Iβ was investigated by DFT calculations, and a mechanism for this transition was proposed. It was found that a large increase in the spacing between the layers was necessary for the phase transition to occur. Furthermore, structural properties of cellulose Iβ were studied by Qian et al. This group developed a theoretical model to explain the size of native cellulose Iβ using molecular dynamics. It was claimed that the hydrogen bonding interaction dominates the interchain interaction, while both hydrogen bonding and van der Waals interaction are important for intersheet interaction. The interested reader should consult the extensive review article by Moon et al. for more information regarding theoretical approaches and results in the modeling of cellulose.

Furthermore, a number of techniques, such as SEM, XPS, ATR-FTIR spectroscopy, and zeta-potential measurements, were used to provide complementary information on the ion adsorption and adsorption mechanism, facilitating the interpretation of the force interaction results and the correlation with computational modeling.

### EXPERIMENTAL SECTION

**Materials.** Spherical regenerated cellulose beads, pure cellulose microspheres (CM), sulfate cellulose microspheres (SCM), and phosphate cellulose microspheres (PCM) (JNC Corporation, Japan) were used for probe particle attachment. The ligand contents of the above cellulose microspheres were 0, 0.9, and 5.0% for CM, SCM, and PCM, respectively. Three-component, solvent-free epoxy resin Araldite CY212 from Agar Scientific Corporation (U.K.) was used to glue the cellulose microspheres to the end of an AFM cantilever. Silica powder with a purity of >99.0% was purchased from Sigma-Aldrich Corporation (USA) and used for zeta-potential measurements. Silver nitrate with purity of >99.8% was purchased from VWR (Sweden) and used to prepare AgNO₃ solution. All other chemicals were used as received, such as NaOH and HNO₃, and were reagent grade (VWR, Sweden). Degassed Milli-Q water was used as a solvent and as a reference liquid in the AFM measurements.

**Methods.** Particle Attachment. Standard V-shaped silicon nitride probes (DNP-10, Bruker, USA) with a spring constant of k = 0.20 ± 0.02 N/m (determined by the thermal tune method using the built-in option in AFM software NanoScope 9.1) were used. To attach the cellulose microsphere (CM, SCM and PCM), the gluing method was employed as described by Leporatti and Dobryden. The whole procedure was monitored through the optical microscope of the AFM.

**Silver Ion Adsorption.** The CM, SCM, and PCM cellulose microspheres were subsequently immersed in aqueous AgNO₃ solution for 1 h at each pH (50 mg/L, at pH 4.3, 5.1, 5.6, and 6.6 successively), followed by filtration and purification with Milli-Q water. After adsorption treatment, the samples were dried and used for spectroscopy characterization.

**Characterization.** Scanning Electron Microscopy. The spherical structure of the cellulose microspheres was studied using SEM (Zeiss Merlin, Germany). The cellulose-microsphere-functionalized AFM probes were dried overnight in air after force measurements and were imaged using SEM. The samples were placed on conductive tape and sputter coated with tungsten. Images were taken, operating at 2.5 kV, and an 8 mm working distance was used. Figure 1 shows the SEM images of CM (a1), SCM (b1), and PCM (c1) utilized in the present work. The cellulose microspheres with a diameter of around 40 μm were selected and attached at the end of the V-shaped cantilever (Figure 1a2, b2, c2). A new cantilever and cellulose microsphere were used in each experiment. The probes were also characterized after attachment.

![Figure 1. SEM images of CM, SCM, and PCM before (a1, b1, c1) and after (a2, b2, c2) attachment of the particles to the V-shaped silicon nitride probe. a3, b3, and c3 are the detailed surfaces of the selected CM, SCM, and PCM particles.](image-url)
force measurements in order to verify that the probes were not removed from the cantilever or were not significantly altered in the working solution with SEM. Also, the detection of adsorbed species on the surface of the cellulose microspheres was performed with SEM measurements using the same experimental conditions as described above.

Zeta Potential. The zeta potentials of silica, CM, SCM, and PCM particles dispersed in 50 mg/L aqueous AgNO₃ solution at various pH values were measured at 25 °C using a Zetasizer Nano ZS, (Malvern, U.K.). The concentrations of all measured samples were the same (0.05 wt %).

Force Measurements with Atomic Force Microscopy. Force measurements were performed with a MultiMode 8 AFM (Bruker, Nanoscope controller, Santa Barbara, CA, USA) equipped with a fluid cell (model MTFM). Circular glass cover slides were used as the silica surface in the force measurements and were cleaned with ethanol and then rinsed with Milli-Q water prior to the measurements. The average surface roughness (Ra) of the glass slide was measured to be 0.8 nm for an area of 500 nm², and the surface contact was on the same spot during each experiment. All experiments were performed at room temperature. The AFM equipped with a liquid cell was operated in contact mode using the Nanoscope 9.1 software. Force curves were acquired to investigate the interaction between the cellulose microsphere probe and a silica surface starting with Milli-Q water as the medium (pH 6.4) and subsequently aqueous AgNO₃ solution (50 mg/L, at pH 4.3, 5.1, 5.6, 6.6). The typical waiting period after a change in the liquid in the fluid cell was 15 min to achieve an equilibrium state. At least 100 force curves were collected for each experiment to obtain good statistics and to minimize the effects from particle geometry and roughness imperfections. Two parallel experiments using new probes and new substrates within one setup were conducted for the CM and SCM system. Three parallel experiments were performed for the PCM system considering the irregular shape of PCM spheres. The experiments gave reproducible results. The experiments were performed for the PCM system considering the irregular shape of PCM spheres. Three parallel experiments using new probes and new substrates within one setup were conducted for the CM and SCM system. All experiments were performed at room temperature. The AFM equipped with a liquid cell was operated in contact mode using the Nanoscope 9.1 software. Force curves were acquired to investigate the interaction between the cellulose microsphere probe and a silica surface starting with Milli-Q water as the medium (pH 6.4) and subsequently aqueous AgNO₃ solution (50 mg/L, at pH 4.3, 5.1, 5.6, 6.6). The typical waiting period after a change in the liquid in the fluid cell was 15 min to achieve an equilibrium state. At least 100 force curves were collected for each experiment to obtain good statistics and to minimize the effects from particle geometry and roughness imperfections. Two parallel experiments using new probes and new substrates within one setup were conducted for the CM and SCM system. Three parallel experiments were performed for the PCM system considering the irregular shape of PCM spheres. The experiments gave reproducible results.

RESULTS AND DISCUSSION

■ COMPUTATIONAL SECTION

The aim of the modeling was to gain more insight and knowledge of binding energies and IR spectra for PO₃-functionalized cellulose and its uptake of silver atoms. Two different model systems were used in the present computational study. First, a system consisting of a cellulose monolayer was made from the crystal structure of cellulose Iβ, taken from the work of Nishiyama et al. The unit cell chosen corresponded to a 2 x 1 monolayer including 84 atoms (Figure 2a). This monolayer was repeated in three dimensions using periodic boundary conditions with a separation of 20 Å to ensure a negligible interaction between the layers. Second, a system consisting of 4 monolayers (336 atoms) was used in order to investigate the ability of silver atoms to form clusters at the functional site (Figure 2b). All calculations were performed with QuantumEspresso version 5.2.0 within the DFT pseudopotential formalism.34

Geometry optimizations were done using the PBE functional and ultrasoft pseudopotentials.35,36 The Grimmes D2 correction37 was included to capture the dispersion interaction, which was especially important for the largest system in this study. IR calculations were performed using the norm-conserving PZ pseudopotentials within the local density approximation8,39 since the vdW interaction was not implemented when using ultrasoft pseudopotentials.

The total energy was minimized according to the BFGS algorithm. The kinetic energy cutoff was set to 80 Ry. In general, convergence criteria were set to 1 x 10⁻⁵ a.u. for the total energy, 1 x 10⁻⁷ a.u. for the forces, and 1 x 10⁻⁷ Ry for the self-consistent energy. For the monolayer, the total energy was sampled using a 1 x 1 x 2 grid generating 2 k points, whereas all calculations based on the large 336-atom system were performed at the gamma point.

■ RESULTS AND DISCUSSION

Surface Characterization. The zeta-potential measurements were carried out on silica, CM, SCM and PCM particles using the Mertz phase correction mode, a Blackman-Harris three-term apodization function, and a zero filling factor of 2. Both the optical bench and sample chamber were under vacuum (1.9 hPa) for each measurement to remove O–H and C=O stretching modes from water vapor and carbon dioxide in the atmosphere. All measurements were repeated at least twice.
dispersed in the aqueous AgNO₃ solution to facilitate the interpretation of the force curves. Figure 3 shows that the three types of cellulose microspheres and silica particles possessed a negative zeta potential in 50 mg/L aqueous AgNO₃ solution and that their zeta potentials decreased with increasing pH. The silica particles had a smaller zeta potential (−66.5 eV, pH 6.63) than the cellulose microspheres and showed the same trends as reported. The zeta potential measured in Milli-Q water for silica particles is 39.5 eV, which agrees with the literature. Although SCM and PCM were modified with negatively charged sulfate and phosphate groups, they had a lower absolute value of zeta potentials than did CM. This is due to the adsorption of Ag(I) ions onto the negatively charged ligands of the cellulose surface. The zeta potential of PCM had the lowest absolute value, indicating that the phosphate-modified cellulose microspheres had a higher capacity to adsorb monovalent silver ions as compared to SCM and CM. This is also well correlated with the higher ligand content for PCM (5%) than for SCM (0.9%).

**Force Spectroscopy Evaluation of the Surface Interactions.**

**Analysis of Force Curves on Approach.** The typical approach and retract force curves for the CM, SCM, and PCM systems are shown in Figure 4. The approach curves (Figure 4A1,B1,C1) demonstrated a clear, strong repulsion at an interaction distance of approximately 100 nm in Milli-Q water (pH 6.4) and was stronger than the interactions in AgNO₃ solution in all three cases, i.e., CM, SCM, and PCM probes. This is in good correlation with the measured zeta potential. This repulsive force can be expected due to the negatively charged cellulose and silica surface interaction in Milli-Q water. After changing to AgNO₃ solution, the long-range repulsive forces remain but are less pronounced than was measured in Milli-Q water as the adsorbed positively charged Ag(I) on the negative functional groups of cellulose particles decreases the cellulose surface negativity. Also, in acidic AgNO₃ solution, H(I) in the solution was expected to partially compensate for the negatively surface charge, leading to a decreased repulsive interaction.

The repulsive term of the DLVO model was successfully fitted to the measured force curves and confirmed that the main contribution to the repulsion between the cellulose and glass surface is due to the double-layer force. (See the DLVO model fitting in Figure 4 and the Supporting Information under S1 for the details of the model fitting.)

The typical AFM approach curves (A1, B1, and C1) and retraction curves (A2, B2, and C2) measured for the CM, SCM, and PCM systems, respectively. The approach curves measured in Milli-Q water (without Ag(I)) as a medium are included for comparison. The solid lines are the DLVO model fits. The average Debye length used in the DLVO model fitting was around 24–26 nm in Milli-Q water, 17 nm from pH 4.3 to 5.6 and 14 nm at pH 6.6 for the CM system, and 23–24 nm for the SCM system and 17 to 13.5 nm for the PCM system. The estimated surface potentials for the cellulose surface were in the range from −9 to −20 mV for the CM system, from −13 to −15 mV for the SCM system, and from −9 to −20 mV for the PCM system. The estimated surface potentials for the glass surface were in the range from −42 to −66 mV. The roughness parameter was set in the range of 1 to 15 nm. (D) Average absolute value of 100 adhesion forces as a function of pH among SCM, PCM, and the silica surface, respectively.
was 17 nm and decreased to 13.5 nm at pH 5.6. However, the Debye length used to achieve the best fit for the SCM system was about 23 nm. Also, the estimated surface potentials from the DLVO fit of the cellulose and the glass surface were lower than the measured zeta potentials but approximately demonstrated the same trends in increasing negativity of both glass and cellulose surfaces with an increase in pH. However, the DLVO model was applied mainly for qualitative analysis of the experimental data since the accurate quantitative analysis of such a surface interaction is complicated when the probe particle possesses irregular probe geometry, as for PCM system, and the cellulose particle is swelled, with a composition that is viscoelastic gel-like or cellulose chains, in an aqueous medium.

An approximate estimation shows that the interaction distances for CM systems decreased from 82 nm in Milli-Q water to around 41 nm in Ag(I) solution, and there was no significant change in the interaction distance as the pH changed from 4.3 to 6.6. For PCM system also the interaction distance, decreased from 65 nm in Milli-Q water to 44 nm in Ag(I) solution) with no clear sensitivity to the pH change. On the contrary, only a small decrease in the interaction distance was observed for SCM system from 66 nm in Milli-Q water to around 59 nm in Ag(I) solution. This can possibly indicate that the screening effect of Ag(I) on repulsive interaction is more pronounced for CM and PCM systems compared to the SCM system (Figures A1 and C1 compared to Figure B1). This is also in agreement with the estimated Debye lengths from the DLVO model. The Debye length is higher for the SCM system than for the CM and PCM systems. This is a bit in contradiction to what is expected, but can possibly related to varying degree of swelling by the cellulose particles. Furthermore, the effect of Ag(I) and their possible interaction or adsorption to the negative functional groups can be observed for the PCM system at pH 6.6. The clear snap-in at an approximate distance of 10 nm indicates that the contribution from the attractive force, most likely due to van der Waals attraction, has increased while the repulsive interaction is partially screened due to the adsorption of positive ions. Thus, this attraction overcomes the cantilever spring constant during the cantilever approach to the negative silica surface and leads to the snap-in. The increase in attraction between PCM particles and the silica surface in AgNO₃ solution at acidic pH can be explained by the high adsorption of Ag(I) to the PCM functional groups. Otherwise, PCM with a strong negative zeta potential should lead only to repulsion when interacting with the silica surface, as follows from Figure 3.

It can be concluded that the interaction among CM, SCM, and PCM probes and the glass surfaces in AgNO₃ solution is mainly governed by the double-layer repulsion force as it follows from the applied DLVO model. The contribution from steric forces can also be expected, regarding the long interaction distances and cellulose swelling. However, the d₀ roughness parameter was used in the DLVO model, which makes it difficult to distinguish the possible contribution from the steric interaction. The repulsive double-layer and steric forces for the cellulose particle—cellulose surface and silica particle—cellulose surface interaction were also previously reported by Holmberg and Rutland. The observed interaction distances, approximately estimated from the force curves in Figure 4 (A1, B1, and C1) falling in the range of 50–100 nm, are in good agreement with the reported references. Meanwhile, the osmotic repulsion force over a small separation distance is expected for such swelled particles.

**Analysis of Force Curves on Retraction.** The retraction curves (Figure 4A2,B2,C2) show diverse behavior for the CM, SCM, and PCM systems. For native CM, no clear pull-out peaks occurred from the retraction curve because of strong repulsive interaction resulting in no adhesion force. The considerable pull-out multiplets on separation were observed for the SCM system. The same phenomenon occurred in Radchenko’s study, and it was interpreted that several cellulose chains adsorbed to the probe during contact and these chains were stretched and progressively detached from the probe particle surface. In the present case, the same trend is observed and indicates the possible detachment or rearrangements of cellulose chains during retraction or the detachment of functional groups. Possible elastic deformation of the swelled cellulose probe also could be one of the reasons for the multiplets in the SCM system (Figure 4 B2), as previously reported in Leporatti’s study. The retraction curves in the case of the PCM system demonstrate no clear deformation or pronounced detachment of cellulose chains and functional groups.

This possibly occurs because of a sharper contact area between the particle and the silica surface since the PCM probe particle is not perfectly spherical and has uneven surface features (SEM image of PCM particles in Figure 1c2). Also, the electrostatic repulsion probably significantly exceeded the attractive van der Waals force and possible weak double-layer attraction due to a small amount of adsorbed positive ions even though H(I) partially affected the charge of the CM surface. The absence of an adhesion force for the native cellulose—silica surface interaction can be thus expected and is in agreement with previously reported results. For the SCM system, Ag(I) can be adsorbed onto the sulfate groups of the SCM particle, leading to an attractive force between the positive Ag(I) and the negative silica surface. Meanwhile, the attractive force between H(I) and the negative silica surface can also contribute to the adhesion force. However, owing to a small ligand content (0.9%), the sulfate groups were almost fully occupied with Ag(I) even at low pH (4.3). Therefore, without an increase in Ag(I) intensity, the adhesion force slightly decreased with a pronounced decrease of H(I) at high pH (Figure 4D). (The schematic representation of the interactions between PCM and the silica substrate in AgNO₃ solution under different pH conditions is shown in section S2 in the Supporting Information.)

In the case of the PCM system, the adhesion force clearly increased from pH 4.3 to pH 6.6 (Figure 4). The increase is expected due to the adsorption of Ag(I) onto PCM since the
concentration of H(I) decreases by a factor larger than 100 in this pH range. Meanwhile, as it follows from the approach curves for the PCM system at pH 6.6 (Figure 4C2), the screened repulsive forces and an increased attraction can most

Figure 5. ATR-FTIR spectra of CM, SCM, PCM with the phosphate region as the inset (A) and ATR-FTIR spectra of PCM before and after adsorption of Ag(I) at various pH values with the phosphate region as the inset (B).

Figure 6. (a) H$_2$PO$_3$ group on the cellulose monolayer. (b) IR spectra for the cellulose monolayer with an H$_2$PO$_3$ group and vibrational modes related only to the functional group at the cellulose monolayer (inset). (c) PO$_3$ group with silver atoms. (d) IR spectra of the cellulose monolayer and the functional group with silver atoms. Vibrational modes related only to the functional group with silver atoms at the cellulose monolayer (inset) and (e) a comparison of IR calculations between the PO$_3$ monolayer with silver atoms (blue lines) and without silver atoms (red lines).
likely lead to the increased adhesion. Also, an attractive 
bridginglike force \(^8\) or binding \(^7\) between the functionalized 
phosphate groups with adsorbed Ag(I) and the negatively 
charged silica surfaces can be expected to contribute to the 
increased adhesion. Furthermore, not many changes in surface 
charge or adsorption ability are expected for the silica surface in 
the studied pH range. Thus, the strongly increased adhesion 
can mainly be related to a higher adsorption of Ag(I) on the 
PCM surface at pH 6.6 than at lower pH values. (The 
schematic representation of the interactions between PCM and 
the silica substrate in AgNO\(_3\) solution under different pH 
conditions is shown in section S3 in the Supporting 
Information.)

Figure 7. XPS survey spectra of CM (A1), SCM (B1), and PCM (C1) and the representative Ag 3d photoemission spectra (inset, left). SEM images of the surfaces of CM (A2), SCM (B2), and PCM (C2) after adsorption (right).

Advanced Spectroscopy and Modeling Evaluation of Adsorption Behavior. The ATR-FTIR spectra of the CM, SCM, and PCM samples (Figure 5) showed main absorption bands in the O−H stretching region between 3600 and 3000 cm\(^{-1}\), the C−H stretching and bending regions around 2900 and 1450 cm\(^{-1}\), respectively, and the strongly band overlapping absorption region below 1400 cm\(^{-1}\).

All samples showed characteristic bands of cellulose. Infrared absorptions between 3600 and 3000 cm\(^{-1}\) are typical for O−H stretching vibrations involved in hydrogen-bonding interactions, and the band with peak intensity at 2892 cm\(^{-1}\) was caused by the C−H stretching vibration. The band at 1642 cm\(^{-1}\) (H−O−H bending) is a clear indication of adsorbed
water in the cellulose samples. This band is stronger in PCM samples than in CM and SCM samples. In addition, overlapping bands due to the infrared absorption of O−H and C−H bending modes as well as C−O stretching vibrations in the glucosidic ring are observed in the wavenumber region between 1400 and 900 cm\(^{-1}\).

Because of the low ligand content and low adsorption of Ag(1), it was hard to find any peak shift or change in line shape in the infrared spectra of CM and SCM microspheres before and after adsorption. However, for the PCM sample the phosphate vibration was clearly affected by Ag(1) adsorption, as shown by the overlapping C−O−P and P−OH stretching vibrations in the 1050−930 cm\(^{-1}\) region. After treatment of the PCM sample with the 50 mg/L AgNO\(_3\) solution at pH values from 4.3 to 6.6, the overlapping C−O−P and P−OH bands shifted to higher wavenumber (inset of Figure 5B). This shift was due to the adsorption of Ag(1) since the shift did not appear by just changing the pH. The result indicates that adsorbed Ag(1) ions interacted with the phosphate group and increased with enhanced pH.

The PCM (H\(_2\)PO\(_4\)−cellulose) and Ag-adsorbed PCM (Ag\(_2\)PO\(_4\)−cellulose) monolayers were relaxed and investigated by IR calculations as shown in Figure 6, where relevant bond lengths are shown. (The CM monolayer was also studied as a reference, and the theoretical IR spectrum is given in Supporting Information S4).

One functional H\(_2\)PO\(_4\) group and the total IR spectra for the PCM monolayer are shown in Figure 6a,b, respectively. All of the strong peaks around 3000 cm\(^{-1}\) can be attributed to O−H stretching modes from cellulose, which confirm the experimental results (Figure 5). The large peak just above 2500 cm\(^{-1}\) is a result of PO−H vibrations from the functional group and oxygen atoms at the cellulose monolayer. When removing all of the peaks caused by the cellulose monolayer, the spectrum becomes a fingerprint of the vibrational modes that appear just because of the functional group, which can be seen in the inset of Figure 6b. The peak at 3200 cm\(^{-1}\) is caused by PO−H stretching vibrations, and all of the peaks around 1000 cm\(^{-1}\) can be assigned to the P−O stretching or PO−H bending vibrations; some of them involve vibrations in the cellulose ring as well. This is also in agreement with experimental data as discussed earlier.

Figure 6d shows the total IR spectra for the cellulose monolayer with two silver atoms on the functional group (Figure 6c). All of the peaks above 2500 cm\(^{-1}\) are a result of O−H stretching vibrations of cellulose. The small peak at 2500 cm\(^{-1}\) is due to C−H stretching vibrations on the cellulose ring, and the strongest peak that can be seen around 1000 cm\(^{-1}\) is a result of the P−O asymmetric stretching vibration. The fingerprint spectra of the functional group with silver atoms are shown in the inset of Figure 6d. No peaks above 1100 cm\(^{-1}\) appear, as all of these peaks are O−H stretching vibrations from cellulose. The strongest peak in Figure 6d (inset) at 1000 cm\(^{-1}\) can be assigned to the asymmetric P−O stretching vibration, which also can be attributed to the peaks at slightly higher wavenumbers. Four peaks can be seen below 1000 cm\(^{-1}\) in which the two at higher wavenumbers can be assigned to P−O asymmetric stretching vibrations and the two at lower wavenumbers are P−O stretching vibrations. This strongly supports the experimental data in Figure 5.

To further explain the shift in wavenumber (as experimentally observed) when silver is coordinated to the functional group, IR spectra in the region between 800 and 1100 cm\(^{-1}\) are shown in Figure 6e, which compares PCM and PCM with adsorbed silver atoms. Peaks A and A′ (symmetric P−O stretch) display a shift toward a higher wavenumber when silver is coordinated to the functional group, whereas peaks B and B′ (asymmetric P−O stretch) display a shift toward a lower wavenumber. The strongest peak C is also assigned to the asymmetric P−O stretching vibration as well as peaks D−G. Interestingly, peaks D and E are shifted toward higher wavenumbers (F and G) when silver is coordinated to the functional group.

Thus, IR calculations show distinct peaks in the spectra when a PO\(_4\) group is present at the cellulose monolayer, in agreement with experimental data, and these peaks will be shifted toward higher wavenumbers when hydrogen is replaced by silver atoms at the functional group, which supports the experimental findings shown in Figure 5.

XPS analysis of CM, SCM, and PCM after Ag(1) adsorption was conducted to study the interaction between the functional groups and the adsorbed Ag(1). Survey XPS spectra of CM, SCM, and PCM are presented in Figure 7A1,B1,C1. The two main peaks (around 533 and 285 eV) shown in the XPS spectra correspond to oxygen and carbon, respectively.

The main C 1s signals for CM, SCM, and PCM were decomposed as shown in Table 1. Four C peaks were detected: C−C/C−H (C1, 285 eV), C−OH (C2, 286 eV), O−C−O (C3, 288 eV), and COOH (C4, 289 eV). S 2p signals at around 533 eV are also shown in Table 1. An examination of XPS spectra of SCM (Figure 7B1) confirmed the presence of traces of sulfur in the spectrum, S 2p at approximately 169.7 eV.

| Table 1. Binding Energy (BE) and Atomic Concentration (AC) of the Elements According to the XPS Spectrum Values of CM, SCM, and PCM after Adsorption |
|---|---|---|---|---|
| CM | BE, eV | AC, atom % | BE, eV | AC, atom % | BE, eV | AC, atom % |
| C 1s | 285.0 | 4.4 | 285.0 | 13.67 | 285.0 | 4.42 |
| 286.8 | 41.41 | 287.2 | 23.6 | 286.8 | 37.57 |
| 288.2 | 11.84 | 286.6 | 5.95 | 288.2 | 7.98 |
| 289.6 | 0.88 | 289.6 | 1.38 | 289.3 | 1.08 |
| O 1s | 533.2 | 38.97 | 533.6 | 26.08 | 533.2 | 39.5 |
| 534.5 | 2.36 | 534.8 | 2.04 | | | |
| Ag 3d\(_{5/2}\) | 368.3 | 0.14 | 368.5 | 0.45 | 367.9 | 1.3 |
| P 2p\(_{3/2}\) | 169.7 | 6.17 | 134.1 | 2.33 | | |

**XPS**

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and S 2s at approximately 230 eV (detectable only in detailed analysis but not visible here). This indicates the presence of −SO₃⁻ groups on SCM as expected. In the same way, XPS spectra of PCM (Figure 7C1) confirmed the presence of traces of phosphor in the spectrum, P 2p at approximately 134.1 eV and P 2s at approximately 190 eV (detectable only in detailed analysis and not visible here), indicating the presence of −PO₃⁻ groups on PCM. Small amounts of Na and Cl were also detected, which might be impurities.

The insets in Figure 7A1,B1 for CM and SCM show the position of all Ag 3d doublet peaks which were at the same binding energies as the standard characteristic metallic Ag⁰ peaks; 3d₅/₂ and 3d₃/₂ have binding energies of 368.2 and 374.2 eV, respectively, showing zero-valent Ag on the surface. However, XPS spectra of the Ag 3d doublet (3d₅/₂ and 3d₃/₂) for PCM were at 368.0 and 374.0 eV (Figure 7C1). Both peaks were shifted about 0.2 eV toward lower binding energies compared to the standard characteristic metallic Ag⁰ peaks. This shift suggests an interaction between Ag(I) and PCM at the nanostructural level. The electronic band structures adjust their energy position when the metal and nonconductor particles attach to each other. The binding energy of monovalent Ag is lower than that of zero-valent Ag⁰, indicating that, in addition to zero-valent elemental Ag, PCM carries monovalent Ag on the surface and at a higher concentration than do CM and SCM, which was also in agreement with zeta-potential results and ATR-FTIR results. Moreover, PCM showed the highest concentration of Ag (1.3%) compared to CM (0.14%) and SCM (0.45%), indicating that more silver accumulated on the surface of PCM than on CM and SCM particles (Table 1). In fact, a low density of nanoscaled Ag particles covered the surfaces of SCM and PCM after force measurements, which was further confirmed by SEM images (Figure 7A2,B2,C2). Most of the Ag nanoparticles are found to have dimensions in the range of 5–50 nm.

The adsorption of metal ions from solutions on the cellulose surface and subsequent reduction to nanoparticles in the presence of entities as aldehyde or carboxylic groups (introduced during bleaching steps) is well documented and is used in in situ metal nanoparticle synthesis. The ether and hydroxyl functions on cellulose or groups such as sulfates and phosphate (introduced by derivatization) facilitate the anchoring of the metal ions tightly onto the fibers via ion–dipole interactions but also after reduction stabilizes the aggregates via surface interactions.55,56 Our earlier studies using XPS have also shown that Ag(I) when adsorbed on nanocellulose became reduced to elemental Ag⁰.16

Below are results, based on DFT modeling, of the energetics of phosphate group attachment to cellulose as well as of Ag(I) adsorption to the phosphate group. The reaction energy \( E_{\text{react H}_2\text{PO}_3} \) for anchoring the H₂PO₃ group to the 84-atom CM monolayer was calculated according to

\[
E_{\text{react H}_2\text{PO}_3} = (E_{\text{H}_2\text{PO}_3\text{-monolayer}} + E_{\text{H}_2\text{O}}) - (E_{\text{cellulose monolayer}} + E_{\text{H}_2\text{PO}_3})
\]

which refers to the reaction when inserting the H₂PO₃ group with phosphoric acid. This reaction energy was calculated to be −278 kJ mol⁻¹, which indicates an energetically favorable reaction. Furthermore, the estimated binding energy \( E_{\text{bind H}_2\text{PO}_3} \) for H₂PO₃ on the cellulose monolayer was calculated to be −448 kJ mol⁻¹ according to

\[
E_{\text{bind H}_2\text{PO}_3} = (E_{\text{H}_2\text{PO}_3\text{-monolayer}}) - (E_{\text{cellulose monolayer}} + E_{\text{H}_2\text{PO}_3})
\]

Similarly, the reaction energy for replacing two hydrogen atoms with silver atoms on the phosphate group was calculated to be −61 kJ mol⁻¹ as the energy difference:

\[
E_{\text{react Ag}} = (E_{\text{Ag}_2\text{PO}_3\text{-monolayer}} + 2E_{\text{H}_2\text{NO}_3}) - (E_{\text{H}_2\text{PO}_3\text{-monolayer}} + 2E_{\text{AgNO}_3})
\]

Comparing the energy differences between the two systems

\[
\Delta E = (E_{\text{Ag}_2\text{PO}_3\text{-monolayer}} + E_{\text{H}_2\text{O}}) - (E_{\text{H}_2\text{PO}_3\text{-monolayer}} + 2E_{\text{Ag}})
\]

gives an energy difference of −191 kJ mol⁻¹.

Finally, the binding energy \( E_{\text{bind Ag}} \) for silver atoms on the PO₃ group with silver was calculated to be −303 kJ mol⁻¹ per silver atom according to

\[
E_{\text{bind Ag}} = (E_{\text{cellulose monolayer}} - Ag_{30}\text{PO}_3) - (E_{\text{cellulose monolayer}} + 2E_{Ag})
\]

The first term refers to Ag-adsorbed PCM, whereas the second term refers to the PCM monolayer and two silver atoms separately outside the system. When using the largest cellulose system with 336 atoms (Figure 8), it was found that 20 silver atoms could easily coordinate to the PO₃ group. Binding energy for the 20th silver atom was −202 kJ mol⁻¹. This energy clearly supports the possibility of further cluster formation of silver at the PO₃-functionalized cellulose surface.

**CONCLUSIONS**

Unmodified and functionalized cellulose microspheres were able to remove Ag(I) from aqueous AgNO₃ solution serving as a model for a contaminated water medium. Force measurement with AFM was demonstrated to be a helpful method for studying the surface interaction between cellulose microspheres and water contaminants such as monovalent silver ions. The zeta-potential values correlated well with the interaction trends for both repulsion and attraction as observed from the force curves. The surface functionality of cellulose, ligand contents, the pH of the medium, and electrostatic interaction between positive and negative particles played a significant role in the adsorption properties of the cellulose microspheres. The AFM
results were further elaborated by extensive spectroscopy investigations.

It was shown here by AFM, XPS, and ATR-FTIR spectroscopy that the surface modification of cellulose microspheres by sulfate and phosphate functionalities improved the adsorption of monovalent silver ions from the aqueous medium. It was also shown that silver ions were reduced to metallic silver on the surface of the modified cellulose particles.

Computational studies reveal a possibility of clustering for Ag(I) to a PO₃-functionalized cellulose surface. A stable structure could easily be obtained for 20 silver atoms. The binding energy when adding the 20th silver atom was calculated to be −202 kJ mol⁻¹, which indicates the ability to coordinate more silver atoms. Calculated IR spectra support the experimental observation of the shifting of P−O stretching vibrations toward a higher frequency upon coordination of silver atoms to the PO₃ group.

The interaction of metal ions and other positive charged species with nanocellulose in an aqueous medium will be the subject of further studies in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b03228.

Parameters used to fit the DLVO model to the experimental data. Schematic representation of the interactions between SCM and the silica substrate in AgNO₃ solution at different pH values. Schematic representation of the interactions between PCM and the silica substrate in AgNO₃ solution at different pH values. IR spectra of the clean cellulose monolayer. (PDF)

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES


