

## EFFECT OF FIXING AGENTS ON THE AMOUNT OF WET END CHEMICALS ADSORBED ONTO A BLEACHED CHEMITHERMOMECHANICAL PULP

LIJUN WANG,<sup>a,b,c,d</sup> LINGZHI LUO,<sup>b,c,d</sup> XINXIN YAN<sup>b</sup> and DANYU WANG<sup>a</sup>

<sup>a</sup>*Department of Light Chemical Engineering, Zhejiang University of Science and Technology, Hangzhou 310023, China*

<sup>b</sup>*Tianjin Key Lab of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China*

<sup>c</sup>*Zhejiang Yongtai Paper (Group) Industry Co., Ltd., Hangzhou 311421, China*

<sup>d</sup>*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China*

✉ *Corresponding author: Lijun Wang, wanglijun@zust.edu.cn*

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For a good performance, most wet end agents used in paper industry must adsorb onto pulp fibers. In this work, we studied the effect of four fixing agents, namely polyamine (PA), polydiallyldimethyl ammonium chloride (PDADMAC), polyethyleneimine (PEI) and a low-molecular-weight and highly cationic starch (LHCS), in promoting the adsorption of some typical wet end chemicals, specifically fluorescence whitening agent (FWA), methyl violet (MV) tinting dye, cationic starch dry strengthening agent (DSA-CS), poly(amidoamine)epichlorohydrin wet strengthening agent (PAE), and cationic polyacrylamide (CPAM) retention agent, onto a bleached chemithermomechanical pulp (BCTMP). It was found that the adsorptions of the wet end chemicals could be improved by all the four fixing agents. When the dosages of the fixing agents were based on the same weight, the LHCS was almost as effective as PA, PDADMAC and PEI, in improving the adsorptions of the negatively charged FWA, and the positively but weakly charged MV and DSA-CS, while it was slightly less effective in enhancing the adsorptions of the highly cationic additives, such as PAE and CPAM. When the dosages of the fixing agents were based on equal charges, the LHCS improved the adsorptions much more than the other three fixing agents. The fact that the LHCS tends to interact more with colloidal substances, while the other three fixing agents interact more with dissolved substances can be used to explain the phenomena discovered.

**Keywords:** fixing agent, adsorption, wet end chemicals, bleached chemithermomechanical pulp (BCTMP), dissolved and colloidal substances (DCS)

### INTRODUCTION

Additives are commonly used in paper industry to improve product properties and process efficiency. For good performance, most of the wet end additives must have good adsorption properties to pulp fibers. Therefore, the topic of additive adsorption to cellulosic fibers has attracted considerable attention over the years.<sup>1-5</sup> Many factors affect the adsorption of additives to fibers, and the main among them might be the presence of highly negatively charged dissolved and colloidal substances (DCS) in pulp and whitewater. Adverse effects of DCS on sizing, wet-strength treatments, and other paper properties have been reported.<sup>6-9</sup> The situation is especially true for cationic additives,

since they are generally adsorbed onto cellulosic fibers through electrosorption.

Fixing agents are often used to neutralize the detrimental DCS and thus to promote the effectiveness of other paper chemicals. For example, a starch-based fixing agent has been used to treat the DCS in a peroxide-bleached thermomechanical pulp and it improves the strengthening effect of subsequently added cationic starch.<sup>10, 11</sup> For a deinked pulp used in newsprint manufacturing, a synergistic effect was found for the addition of polydiallyldimethyl ammonium chloride (PDADMAC) followed by a cationic polyacrylamide (CPAM) retention agent. This combination of additives provided a better control of microstickies than the addition of PDADMAC or CPAM alone.<sup>12</sup>

Polyaluminum chloride (PAC), polyamine (PA), polyamidoamine-epichlorohydrine (PAE), polyethyleneimine (PEI), and PDADMAC were used to control the DCS in an alkaline peroxide bleached mechanical pulp (APMP), and they were found to promote to various extent the sizing efficiency of AKD under neutral conditions.<sup>13</sup>

However, unexpected results have also been reported. For example, it was found that for a bleached chemithermomechanical pulp (BCTMP), PDADMAC is effective in retaining a rosin size in the presence of DCS, but it is not effective at all in promoting sizing, possibly because DCS preferably adsorbs on the size particles.<sup>14</sup> A recent study reported that when a polyamine fixing agent was used to pretreat a deinked pulp, the effectiveness of a subsequently-added CPAM strength agent was unexpectedly decreased, while that of an anionic polyacrylamide (APAM) strength agent was increased. The contradictory reports indicate a lack of understanding of fixing agents and suggest that a further study of their adsorption amount or even the morphology of the chemicals being absorbed is required. Unfortunately, literature references on this subject are very limited.

In our previous study, we have shown that a low-molecular-weight, highly cationic starch (LHCS) can counteract the negative effect of DCS and improve the adsorption of some typical wet end chemicals.<sup>15, 16</sup> When a bleached chemithermomechanical pulp was pretreated with such a LHCS, i.e., starch-based fixing agent (SBF), the adsorptions of fluorescent whitening agent, tinting dye, wet strengthening agent, dry strengthening agent, neutral sizing agent, and retention agent onto fibers were all improved, and the improved adsorptions resulted in higher brightness, better tinting, higher wet and dry strengths, better sizing, and higher retention and drainage.<sup>16</sup> Considering that different fixing agents may behave quite differently and it is often necessary to select a proper fixing agent to control the DCS for a given pulp, in this work, three synthesized fixing agents, polyamine (PA), polydiallyldimethyl ammonium chloride (PDADMAC) and polyethyleneimine (PEI), as well as LHCS, were investigated as promoters of the adsorptions of five wet end chemicals, namely fluorescence whitening agent, tinting dye, wet strength agent, dry strength agent and retention agent.

## EXPERIMENTAL

### Materials

The pulp used in this study was a mixed hardwood bleached chemithermomechanical pulp (BCTMP)

refined to a Canadian Standard Freeness of 490 mL. The BCTMP was supplied by Shandong Zhengda Papermaking Company, China. The fixing agent LHCS, with the degree of substitution (DS) of 0.65, and the charge density of 2.50 meq/g, was prepared in our own laboratory by reacting amylopectin starch (Ting Hsin International Group, Tianjin, China) with epoxypropyltrimethyl chloride, followed by acidic hydrolysis.<sup>15, 17</sup> The fixing agents PA, PDADMAC and PEI used in this study were commercial products with positive charges of 6.36, 6.70, and 13.30 meq/g solid, respectively, from Shandong Linyi Fine Chemistry Co. Ltd., Shandong Luyue Chemical Co. Ltd., Province, and Hubei Wuhan Qianglong New Chemical Materials Corporation, China.

Other wet end chemicals, included diamino-stilbenesulfonate fluorescent whitening agent (FWA, from Zhejiang Transfar Whyon Chemical Co. Ltd., China), methyl violet tinting dye (MV, from Tianjin Li'ang Dyestuff Co. Ltd., China), cationic starch dry strength agent (DSA-CS, from Zhejiang Hangzhou Papermate Science & Technology Co. Ltd., China), poly(amidoamine)epichlorohydrin wet-strength agent (PAE, from Shandong Cailun Shenxing Chemical Co. Ltd., China), and cationic polyacrylamide retention agent (CPAM, dry powder, average molecular weight around 4 million, from Beijing Angel Specialty Chemical Co. Ltd., China). Regarding charge properties, the FWA was slightly negative, the MV was slightly positive, while PAE, DSA-CS and CPAM had positive charges of 2.30, 0.43 and 1.53 meq/g solid.

### Methods

The BCTMP was diluted to 1% consistency, and 1 g/L solution of a fixing agent was added. The pulp slurry was gently stirred for 30 s, and then a diluted solution of a wet-end chemical was added in a corresponding dosage as follows: FWA 0.67%, MV 0.004%, DSA-CS 1.0%, PAE 0.4%, and CPAM 0.05%, all reported as the weight of dry chemical to the weight of oven-dried pulp. The pulp slurry was stirred for another 30 s, centrifuged at 2000 rpm for 5 min, and the supernatant was taken to determine the concentration of the residual chemical by UV-visible spectroscopy.<sup>16</sup> In our experiments, the fixing agents themselves are adsorbed almost completely and their residues in the supernatant are very limited. As a result, the contribution of fixing agents to UV-visible absorbance was negligible and the absorbance of the supernatant measured at the typical wavelength was mainly the contribution of the residual wet end chemical.<sup>18</sup> One exception was the effect of LHCS pretreatment on the adsorption of DSA-CS, where the absorbance resulting from residual LHCS has been deducted.<sup>19</sup>

The difference between the amount of the additive initially added and its residual amount was calculated as the additive adsorbed onto the fibers, and the

adsorption ratio was calculated as the ratio of the adsorbed additive to the initially added additive.

## RESULTS AND DISCUSSION

### Effect of fixing agents on the amount of chemicals adsorbed onto BCTMP

As fixing agents had different charge densities, two dosing conditions were studied: one based on equal weight percentage (weight of the chemical on the weight of oven-dried pulp) and another based on equal charge amount ( $\mu\text{mol/g}$ ). The results for these two addition rates are marked as (a) for weight-based and (b) for charge-based addition in Figures 1 to 5. In the following, the effect of the examined fixing agents on the adsorption of five selected additives is presented.

FWAs are commonly used to improve the brightness of paper products, but they are rarely used in lignin-containing products. However, some studies showed that FWA can improve the brightness stability of BCTMP.<sup>20</sup> On the other hand, BCTMP is known to contain high amount of DCS, which may interfere with the adsorption of FWA onto fibres,<sup>21</sup> but the reasons are not well explained. Our opinion is that FWA, although weakly anionic, can be easily adsorbed onto fiber for two reasons: first, due to the intermolecular forces between its triazinyl groups and cellulose hydroxyl groups, secondly, owing to the anchoring effect of some divalent ions, typically calcium ion in the disulfonate group of FWA and the carboxyl group of cellulose. Most of the dissolved and colloidal substances, being very negative, repel FWA molecules from being adsorbed onto cellulose. In addition, DCS has the priority to bind the calcium ions that are present in the pulp. Therefore, it is reasonable to believe that a higher amount of DCS impedes the adsorption of FWA onto fiber. With such thinking, it becomes interesting to verify if the FWA adsorption can be improved by the fixing agent pretreatment of pulp, which reduces the amount of DCS.

The above thinking is proved by the results shown in Fig. 1 (a), where the adsorption ratios of FWA are clearly seen as being increased by each of the four fixing agents pretreatments with LHCS, PA, PDADMAC and PEI (the increments ranged from 76% to more than 85%). However, it is also seen that further increasing the dosage of fixing agents incurred less improvement of FWA adsorption. As it is well-known that FWAs are easy to agglomerate by cationic polymers, the reduced adsorption was ascribed to the formation

of FWA agglomerates, which are not well retained onto fiber.

Another phenomenon seen from Fig. 1 (a) is that based on dosages of equal weight, the LHCS was no worse than the PA, PDADMAC and PEI, although it had a much lower charge density. In contrast, when used in equal charge, as shown in Fig. 1 (b), the LHCS performs better than the other fixing agents tested in this study.

The second chemical we investigated was methyl violet tinting dye. This additive is often used in a very small amount to offset the yellowish color of pulp, so paper products look whiter. Chemically, it is a basic dye with weak cationic charge, so it may be strongly influenced by DCS, or in other words, reducing the amount of DCS by fixing agent pretreatment may increase its adsorption. The speculation is proved in Fig. 2 (a) and Fig. 2 (b), where increased adsorption of MV is seen for all the fixing agent pretreatments, and increasing the fixing agent dosage resulted in increased adsorption. Again, at the same weight dosage (Fig. 2 (a)), the effect of LHCS was similar to those of the other three fixing agents.

The third additive considered was a cationic starch dry strength agent (DSA-CS). The degree of substitution for traditional cationic starch strength agents is around 0.02-0.04. Slightly different from that, the DSA-CS used in this study had a DS around 0.07, and its charge density was around 0.43meq/g. The aim of this special cationic starch design was to improve its resistance to DCS. Because of its high charge, the new DSA-CS itself had a good adsorption to BCTMP fibers. This is evident from Fig. 3, which shows its adsorption ratio as high as 91% when the dosage was 1%. Despite that, its adsorption ratio was further increased with the use of the fixatives.

The results in Fig. 3 show that the LHCS was an excellent fixing agent, also promoting the adsorption of DSA-CS, even though it had a lower charge density than PA, PDADMAC and PEI. The phenomena of DSA-CS seen from Fig. 3 (a) and Fig. 3 (b) are very similar to those of MV seen from Fig. 2 (a) and Fig. 2 (b), indicating that an explanation applicable to both of these two chemicals might exist.

Next, the adsorption of PAE wet strengthening agent was studied. Unlike FWA, MV, and DSA-CS, PAEs used to improve wet strength of paper are often designed to have medium to high cationic charges, and sometimes PAEs themselves can be used as a fixing agent, although their

charge densities are generally lower than the common ones (for example, in this study, the PAE had a charge density of 2.30 meq/g solid, while the PA, PDADMAC, PEI had the charge density 2-5 times higher). The way adsorption of this additive is affected by the fixing agent

pretreatments is shown in Fig. 4. We see that without fixing agent pretreatment, the adsorption ratio of PAE is only 68%, but with the pretreatments, the adsorption ratios significantly increase.

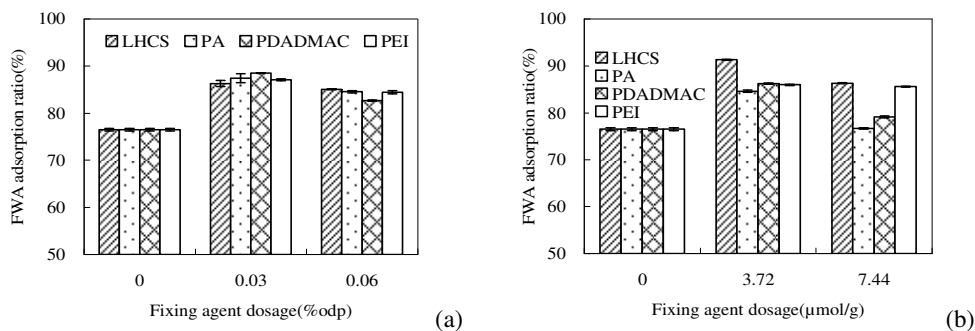


Figure 1: Effect of pulp pretreatments by different fixatives on the adsorption of FWA added at 0.67% with respect to pulp. Fixing agents added (a) in equal quantity; (b) at equal charge

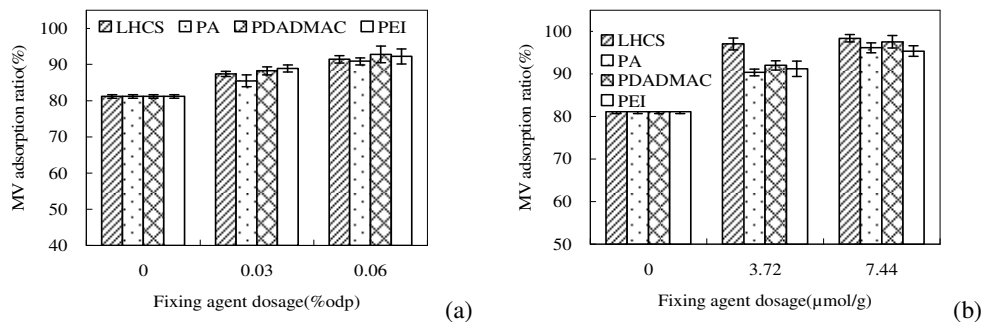


Figure 2: Effect of pulp pretreatments by different fixatives on the adsorption of MV added at 0.004%. Fixing agents added (a) in equal quantity; (b) at equal charge

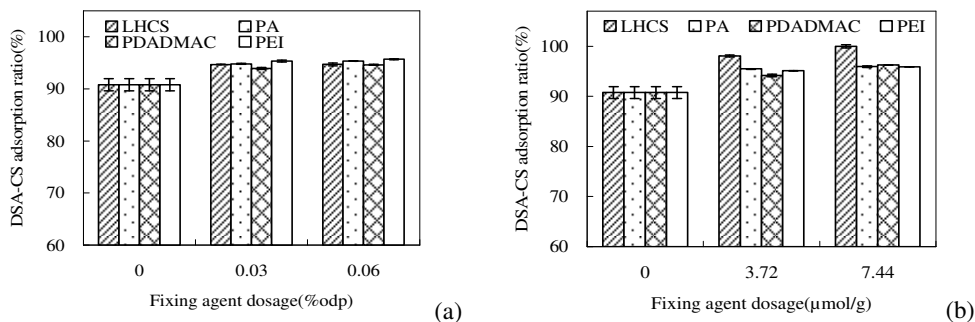


Figure 3: Effect of pulp pretreatment by different fixatives on the adsorption of DSA-CS added at 1%. Fixing agents added (a) in equal quantity; (b) at equal charge

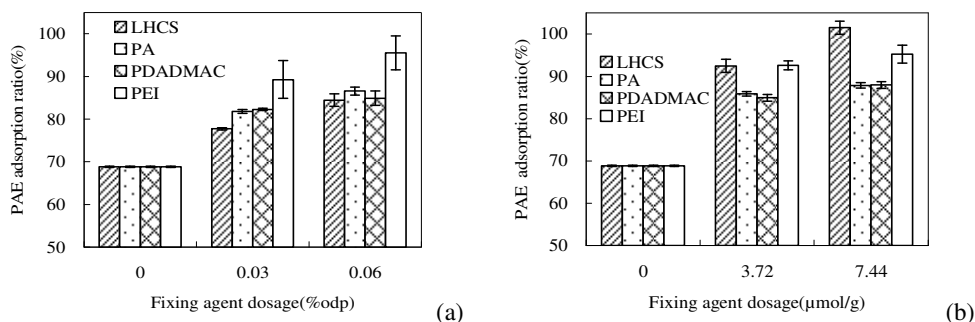


Figure 4: Effect of pulp pretreatments by different fixatives on the adsorption of PAE added at 0.4%. Fixing agents added (a) in equal quantity; (b) at equal charge

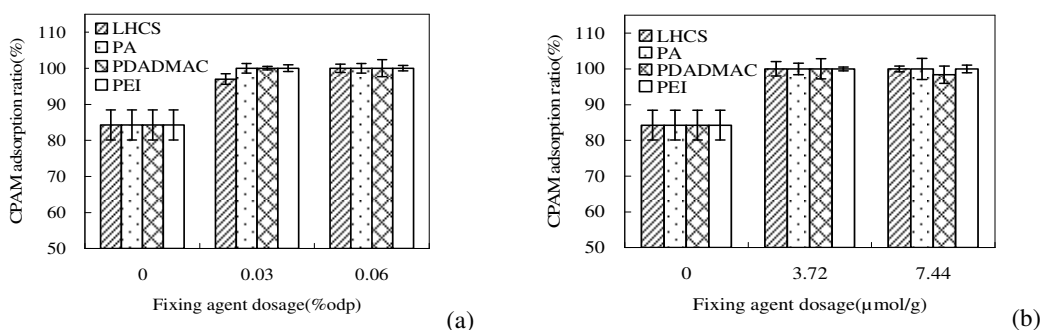


Figure 5: Effect of pulp pretreatment by different fixatives on the adsorption of CPAM added at 0.05%. Fixing agents added (a) in equal quantity; (b) at equal charge

Clearly different from the results in Figs. 1, 2 and 3 was the effect of pretreatment when fixing agents were added at similar weight ratios. Under these conditions, the improvement of PAE adsorption by LHCS was much worse than those resulting from pretreatments by the other three agents. Interestingly, this time it was found there was a good correlation between the charge densities of the fixing agents and their performance. When the fixing agents were added on same charge bases (Fig. 4 (b)), the effect of LHCS was found to be the best again.

Finally, the adsorption behavior of CPAM was investigated. Fig. 5 showed that when the dosage of CPAM was fixed at 0.05% (a representative dosage in practical papermaking systems) without fixing agent, its adsorption ratio onto BCTMP was only about 85%, but it could be improved to nearly 100% when the fixing agent was used.

Fig. 5 also shows that at a low dosage of 0.03%, the LHCS was slightly inferior to PA, PDADMAC and PEI (Fig. 5 (a)), while at a high dosage of 0.06%, or at 3.72  $\mu\text{mol/g}$  and 7.44  $\mu\text{mol/g}$  (Fig. 5 (b)), no difference was seen among the four fixing agents, as they all increased the adsorption ratio to nearly 100%. The slight

inferiority of the LHCS to PA, PDADMAC and PEI at the dosage of 0.03% was again ascribed to the fact that less DS can be reduced by LHCS, and CPAM is liable to be affected by the DS.

#### Explanation on different performance of LHCS and of the other fixing agents

From the above discussion, it can be seen that when the dosages of the fixing agents were based on the same weight, the LHCS was almost as effective as PA, PDADMAC and PEI, in improving the adsorptions of the negatively charged FWA, and the positively but weakly charged MV and DSA-CS, indicating that for the adsorption of these three chemicals, the charge density of fixing agent was not the only important factor. The negligible differences in the adsorption improvements by the PA, PDADMAC and PEI, in spite of the big difference in their charge densities (notice especially the high charge density of PEI), are further evidence for this conclusion. But for enhancing the adsorptions of the highly cationic additives such as PAE and CPAM, the LHCS was slightly less effective. However, when the dosages of the fixing agents were based on equal charges, the LHCS improved

the adsorptions much more than the other three fixing agents.

To explain the above phenomena, we started from the fact that the neutralization ability of LHCS is much lower than those of the other three fixing agents (because the charge density of LHCS is much lower than those of the others). Combining the results of one of our earlier studies indicating that at the same weight-based dosage, the LHCS interacts more with the colloidal substances, while the other fixing agents interact more with the dissolved substances<sup>[22]</sup>, it is thought that the adsorptions of FWA, MA and DSA-CS are not significantly affected by the dissolved substances (or in other words, the adsorptions of FWA, MA and DSA-CS are more significantly affected by the colloidal substances), while those of PAE and CPAM are significantly affected by dissolved substances. The conjectures are thought to be reasonable based on the analysis below.

First, both FWA and MV are small molecule products, so they are generally not significantly affected by the dissolved substances, which in most cases are also composed of small molecular-weight components. Second, both FWA and MV have strong affinity to anionic surfaces including CS surfaces, thanks to the Van der Waals force between the additives and the anionic surfaces (for FWA, its adsorption to anionic surfaces can be further improved by the calcium anchoring effect). For DSA-CS, with its molecular weight being relatively high and charge density relatively low (0.43 meq/g), it preferentially bridges CS particles like a retention aid, when it is added into a DS- and CS-containing pulp furnish. On the other hand, as regards PAE and CPAM, their adsorptions are prone to be affected by DS, since their charge densities are high (2.30 meq/g for PAE, and 1.53 meq/g for CPAM). Interestingly, the difference between these two chemicals can be easily found: as can be seen from Fig. 4 (a) and Fig. 5 (a), at the dosage of 0.03%, the adsorption of PAE is more severely affected by different fixing agent pretreatments. The reason is that CPAM, as a typical retention agent, has a higher tendency to flocculate colloidal substances through the bridging mechanism (in this aspect, it is similar to DSA-CS), i.e., compared with PAE, its adsorption is more affected by colloidal substances.

Once we admit that the adsorptions of FWA, MA and DSA-CS are more significantly affected by the colloidal substances, while those of PAE

and CPAM are more significantly affected by the dissolved substances, combining our early finding that LHCS interacts better with colloidal substances than with dissolved substances, it becomes very easy to understand that at the same weight-based dosage, the LHCS is similar to the other fixing agents in promoting the adsorptions of FWA, MA, and DSA-CS, but it is inferior to the other three fixing agents in promoting the adsorptions of PAE and CPAM. Even more, it can also explain the phenomenon that at the same charge-based dosage, the effect of LHCS was the best, in that, under such conditions, the LHCS neutralizes a similar amount of DS as the other fixing agents do, yet it does a better job in removing CS than the other fixing agents, since at the same charge-based dosage, the corresponding weight-based dosage for the LHCS is higher.

## CONCLUSION

This study demonstrated that fixing agent pretreatment was an effective way to improve the adsorption of wet end chemicals onto a BCTMP pulp. The adsorption of the wet end chemicals, such as fluorescent whitening agent (FWA), methyl violet (MV) tinting dye, poly(amidoamine)epichlorohydrin (PAE) wet strengthening agent, cationic starch dry strength agent (DSA-CS), and cationic polyacrylamide (CPAM) onto the BCTMP can be improved by all the four fixing agents used in this study, namely LHCS, PA, PDADMAC and PEI. When the dosages of the fixatives were based on weight, the LHCS was almost as effective as the other three additives in improving the adsorption of the anionically charged FWA, or cationically but weakly charged MV and DSA-CS. For enhancing the adsorptions of the highly cationic additives, such as PAE and CPAM, the LHCS was slightly worse. When the dosages of the fixing agents were based on equal charges, the LHCS was much better than PA, PDADMAC and PEI. The above phenomena can be explained by two facts: (1) The LHCS tends to interact more with colloidal substances, while the other three fixing agents interact more with dissolved substances; (2) The adsorptions of FWA, MV and DSA-CS are not significantly affected by dissolved substances, while the adsorptions of PAE and CPAM are.

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