A New Method for Paper Conservation: Triple Mixture of Methyl Cellulose, Carboxymethyl Cellulose and Nano-Micro Calcium Hydroxide Particles

Kâğıt Eserlerin Konservasyonunda Yeni Yöntem: Metil Selüloz, Karboksimetil Selüloz ve Nano-Mikro Kalsiyum Hidroksit Partikülleri Üçlü Karışımı

Research Article

Mehmet Konuklar*, Mehmet Saçak
Ankara University, Department of Chemistry, Ankara, Turkey

ABSTRACT

In this study, a new method was developed for combining deacidification and strengthening steps of paper conservation, by using triple mixture containing *methyl cellulose, carboxymethyl cellulose and nano-micro calcium hydroxide particles* in suitable ratios. This new method was developed by investigating the effects of the triple mixture at different ratios on deacidification and mechanical strength of paper samples before and after thermal ageing. It was observed that the triple mixture containing 1% (w/v) methyl cellulose, 1% (w/v) carboxymethyl cellulose and 1% (w/v) nano-micro calcium hydroxide particles neutralized acidic substitutes in paper, formed enough amount of alkaline reserve and increased tensile strength of paper by 100 %. The mechanical strength of paper samples before and after thermal ageing was evaluated by tensile strength, folding endurance and whiteness tests. SEM pictures were also used for characterizations. The deacidification quality of new method was evaluated together with alkaline reserve, surface pH and pH of aqueous extracts.

Key Words
Paper conservation, Deacidification, Nanoparticles, Calcium hydroxide.

ÖZET

Bu çalışma ile, uygun oranda *metil selüloz*, *karboksimetil selüloz* ve *nano-mikro kalsiyum hidroksit partikülleri* içeren üçlü karışım kullanılarak, kâğıt konservasyonundaki deasidifikasyon ve sağlamlaştırma aşamalarını birleştiren yeni bir yöntem geliştirilmiştir. Yeni yöntem, değişik oranlardaki üçlü karışımın, kâğıt örneklerinin ısıl yaşlandırma öncesi ve sonrası deasidifikasyonu ve mekanik dayanımı üzerine etkisi incelenerek geliştirilmiştir. %1(w/v) metil selüloz, %1(w/v) karboksimetil selüloz ve %1(w/v) nano-mikro kalsiyum hidroksit partikülleri içeren üçlü karışımın, kağıdın pH değerini 9 civarına çıkartarak kağıtta yeterli miktarda alkali rezerv oluşturduğu ve kağıdın çekme dayanımını %100 arttırdığı gözlemlenmiştir. Kâğıt örneklerin mekanik dayanımı; çekme dayanımı, katlama dayanımı ve beyazlık testleriyle değerlendirilmiştir. Ayrıca SEM fotoğrafları karekterizasyon için kullanılmıştır. Yeni yöntemin asitten arındırma özelliği ise alkali rezerv tayinleri, yüzey pH ve sulu ekstrakt pH analizleri ile değerlendirilmiştir.

Anahtar Kelimeler
Kâğıt Konservasyonu, Deasidifikasyon, Nanopartiküller, Kalsiyum Hidroksit.

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Correspondence to: Mehmet Konuklar, Ankara University, Faculty of Science, Department of Chemistry, Tandoğan Campus, Ankara-Turkey
Tel: +90 312 212 62 00 Fax: +90 312 223 04 51 E-Mail: konuklar@hotmail.com

INTRODUCTION

Acidity which is the most important problem [1] of libraries nowadays, cause serious deteriorations to paper work of arts. By the time, acidic papers became darken and brittle [2,3]. As a result of the paper degradation studies, it was found out that acidity catalyze and speed up the hydrolysis of cellulose [4] and for this reason many paper conservation researchers focused on the sources of acidity. The studies carried out showed that paper alum [$Al_2(SO_4)_3$] [5,6] used commonly between 1840 and 1990 in the manufacture of paper, lignin [7], acidic inks [8], atmospheric contaminants and adhesives [9] caused formation of acids in paper work of arts.

The border for the negative effects of acidity on paper work of arts is accepted as pH values under 6.2 [10] and a consensus was reached that deacidification of papers should be carried out under this pH value. Increasing the pH value to around 8.5 by neutralizing acids in the structure of paper, increasing the amount of alkaline reserve over 400 mmol/kg and preventing paper from becoming acidic again by removing undesirable substances from paper are purposed by deacidification [11].

Various chemicals or their mixtures were used for the deacidification of paper work of arts and different deacidification methods were developed [12]. Especially, $Ca(OH)_2$ is effective for the deacidification of paper work of arts and it preserves the mechanical strength of paper without causing any discoloration [13-15]. Rodorico et al. [16] showed that 1% nano-micro $Ca(OH)_2$ particles in alcohol could be used for the deacidification of paper. Sequeira et al. [17] used aqueous saturated $Ca(OH)_2$ solution and nano $Ca(OH)_2$ particles dispersion in isopropanol separately for the deacidification of paper work of arts with iron gall ink and they were found that nano $Ca(OH)_2$ particles dispersion in isopropanol was more effective for paper deacidification.

After the deacidification process applied to deteriorated paper objects arts, generally a strengthening process is applied as a second step [18]. Using cellulose ether solutions is a generally accepted method for strengthening process [19,20]. Austrian National Library developed a process for deacidification and strengthening aged newsprint on a large scale involving the simultaneous application of 0.8% $Ca(OH)_2$ and 1% methyl cellulose (MC) [21].

In this study, combining the deacidification and strengthening steps in paper conservation was purposed by using first time the triple mixture of $Ca(OH)_2$, MC and carboxymethyl cellulose (CMC) at suitable ratios. Furthermore, more effective deacidification was achieved by keeping the size of $Ca(OH)_2$ particles at nano-micro levels in triple mixtures.

MATERIALS AND METHODS

Materials

Whatman No:1 filter paper manufactured from 100% cellulose and containing no additives was used in the study. Sodium hydroxide (Merck), calcium hydroxide (Merck), calcium chloride, CMC (Purity: 99,6%, viscosity (2% hoeppler) 10500cp, DS: 0.8, Acıselsan AŞ) and MC (Purity: 99,3%, viscosity (2% hoeppler) 4500cp, DS: 1.7, Atlantis France) were used as they received.

Procedures

Nano and microparticles of $Ca(OH)_2$ were synthesized by controlled mixing of NaOH and $CaCl_2$ solutions at 90°C (16,17). The mixture in the form of suspension was cooled to room temperature under nitrogen atmosphere to prevent the carbonization of $Ca(OH)_2$ particles. Than the suspension was washed with saturated $Ca(OH)_2$ solution for four times to decrease the amount of NaCl in the suspension. It was mixed for 1 h in an ultrasonic bath and then kept in an oven for 24 h at 40°C. $Ca(OH)_2$/water ratio (g/g) was measured as 8/10.

CMC and MC mixtures at different ratios were prepared by taking suitable amounts of CMC and MC in powder form to determine optimum CMC/MC ratio in triple mixtures. These mixtures were dissolved in saturated $Ca(OH)_2$ solution so as to be the total concentration of CMC and MC in the solution was 2% (w/w). The mixtures were left to wait for 24 h in room conditions for homogenization.

MC becomes agglomerated in saturated $Ca(OH)_2$ solutions at room temperature. For this reason, for the preparation CMC/MC mixture at 00/100 ratio, an amount of $Ca(OH)_2$ solution saturated at room temperature was heated to 80°C and 2 g MC was dissolved in it. Then the volume was completed to 100 mL with cold saturated $Ca(OH)_2$ solution.

The triple mixtures prepared as described above were applied uniformly to both surfaces of 4 Whatman No:1 filter papers with dimension of 46 x 57 cm. Totally 50 mL triple mixture was used for both surfaces of each filter paper. After the application of triple mixture, the filter papers were first left to wait in air for 2 h and than dried by being pressed between hollytex and drying cardboard for 72 h. For each samples group containing 4 filter papers, two papers were subjected to accelerated ageing process, while the other two were kept under room conditions for comparison. For accelerated ageing process, papers were kept in an ageing chamber at 105°C for 24 days in accordance with TS 4839 ISO 5630-1 standard [22].

For the determination of ideal $Ca(OH)_2$ ratio in triple mixtures, mixture of 1% MC and 1% CMC were selected (CMC/MC ratio in the mixture is 1 and total concentration of CMC and MC is 2%) and triple mixtures containing different amounts of $Ca(OH)_2$ were prepared by using this constant CMC-MC mixture ratio. The application of mixtures to papers and accelerated ageing processes were carried out as described above.

Characterization

Tensile strength tests were carried out in accordance with TS 3123-2 EN ISO 1924-2 standard [23] by using Lloyd Instruments LR5 K. Rate of elongation and loading were adjusted as 20 mm/min and 500 N respectively.

Folding endurance tests were carried out in accordance with TS 5162 ISO 5626 standard [24] by using Tinius Olsen Folding Endurance Tester. 1 kg load was applied for all folding endurance tests.

Whiteness tests were carried out with Konika Minolta Spectrophotometer CCM-3630 by using Cutoff UV 100 % measurement model and White Calibration Plate No: 17441002.

Alkaline reserve determinations were carried out by back titration of excess HCl added into sample with NaOH according to TS ISO 10716 [25]. pH determinations of aqueous extract were carried out in accordance with TS 4842 standard [26].

Orion 8235BN flat surface electrode was used for surface pH measurements. In the measurements carried out under room conditions, first 1-2 drops of distilled water were dripped on the surface of paper, than the electrode was attached on the paper surface and the first value

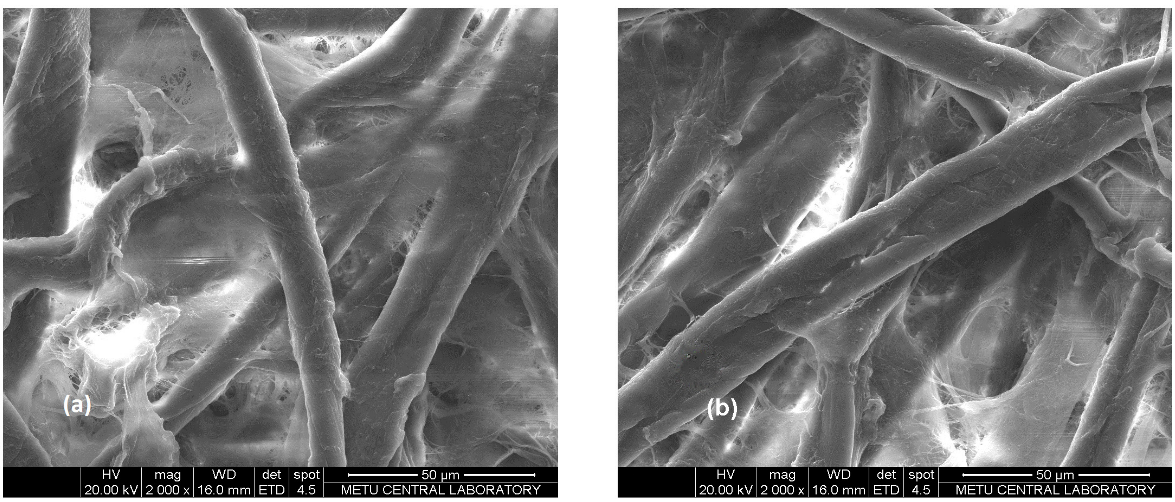

Figure 1. SEM images of Whatman No:1 filter papers before (a) and after (b) thermal ageing.

become constant on the pH meter was recorded. Measurements were performed two times and average of two measurements was taken as the surface pH value.

Size distribution of $Ca(OH)_2$ particles in suspension was measured by Mastersizer 2000 instrument. For the determination of distribution and sizes of $Ca(OH)_2$ particles on paper surface, SEM images of papers were obtained by using QUANTA 400F Field Emission instrument.

RESULTS AND DISCUSSION

Effect of thermal ageing on paper

SEM images of Whatman No:1 filter papers before (Figure 1a) and after ageing (Figure 1b) were shown in Figure 1. Ageing process was applied by keeping paper samples at 105°C for 24 days. Since this process is based only on temperature change, it does not represent the real ageing environment as emphasized by Havlínová et al [27]. However, it can be seen that such ageing application cause breakages in paper fibers in the direction of their length and it has been known that such fiber breakages decrease the folding endurance of paper [28].

Determination of suitable carboxymethyl cellulose/methyl cellulose ratio

Solutions with CMC/MC ratio of 00/100, 25/75, 50/50, 75/25 and 100/00 were prepared in saturated $Ca(OH)_2$. Total amount of CMC/MC in these solutions was adjusted so as to be 2% by mass. These 5 solutions were applied to paper samples and their effects on tensile strength, folding endurance, whiteness, alkaline reserve, pH values of aqueous extract and surface of papers were determined before and after ageing.

Tensile strength data of paper samples before and after ageing process were shown in Figure 2. Each triple mixture tested increased the tensile strength of paper approximately from 2500 N/m to around 5000 N/m. Tensile strength of the papers subjected to saturated $Ca(OH)_2$ solution containing 2% pure MC (CMC/MC ratio is 00/100) is slightly higher than that of the papers subjected to saturated $Ca(OH)_2$ solution containing same amount of pure CMC (CMC/MC ratio is 100/00). This observation supports the fact determined also by other researchers [9,19,20] that MC is more effective than CMC for paper conservation.

For the effect of CMC/MC mixtures on tensile strength of paper, the highest tensile strength was obtained as 5112 N/m for 50/50 mixture. The increase in tensile strength at this ratio was thought to be originated from the synergistic effect of MC and CMC, and the synergistic effect of the triple mixture having 50/50 CMC/MC ratio is higher than that of the mixtures with 25/75 and 75/25 CMC/MC ratios.

Effect of CMC/MC mixing ratio in triple mixture on the folding endurance of papers was examined in a separate experiments set and the data shown in Figure 3 was obtained. The highest folding endurance was obtained with saturated $Ca(OH)_2$ solution containing 2% MC with 387 folds, and it was observed that folding endurance decreased with increasing CMC ratio and decreased down to 340 folds for 2% CMC.

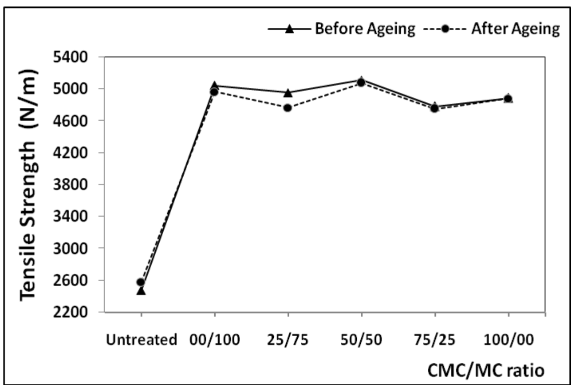

Figure 2. Effect of CMC/MC ratio in triple mixture on tensile strength of paper.

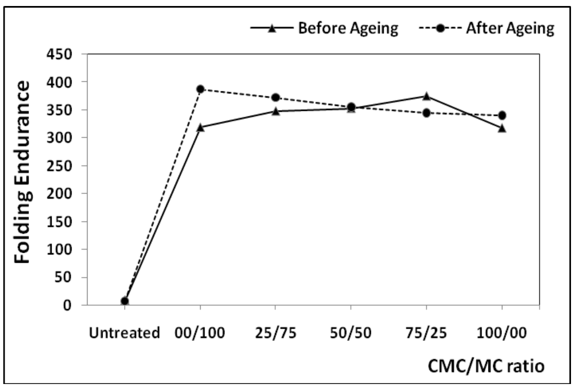

Figure 3. Effect of CMC/MC ratio in triple mixture on folding endurance of paper.

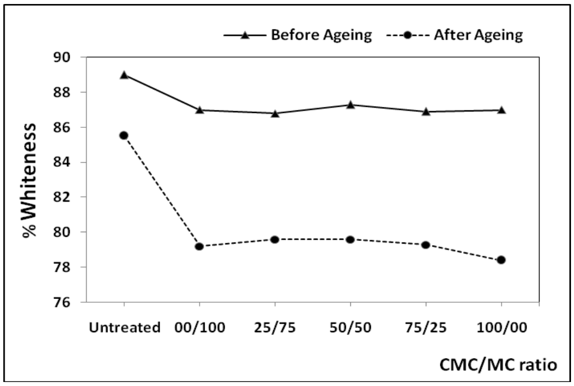

Figure 4. Effect of CMC/MC ratio in triple mixture on whiteness of paper.

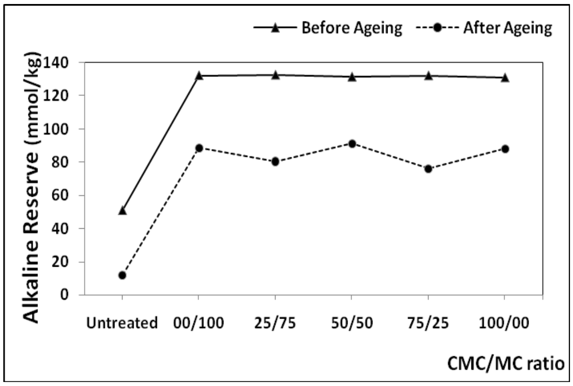

Figure 5. Effect of CMC/MC ratio in triple mixture on alkaline reserve of paper.

As can be seen from Figure 4, due to the transparency of cellulose ethers and white colour of $Ca(OH)_2$, triple mixtures used in the experiments caused approximately 2% decrease in the whiteness of papers without being dependent on CMC/MC ratio. The whiteness of papers subjected to triple mixture decreased approximately 7.5% with ageing, while the whiteness of unprocessed papers decreased only 3.5%. The reason for this is that the oxidation products which are formed after ageing and decrease the whiteness of papers, formed much more when triple mixtures are used, as also indicated by Arney and Jacobs [29].

Decrease in whiteness increases with ageing and when CMC/MC ratio approaches to 50/50, the effect of ageing on whiteness decreases relatively. In the mixtures formed with $Ca(OH)_2$ and CMC, number of carbonyl groups formed after ageing increase [30] and whiteness of paper decreases more than that of the papers treated with other mixtures.

The triple mixtures tested increased the alkaline reserve of papers from 50 mmol/kg to 130 mmol/kg (Figure 5) independent of CMC/MC ratios because the CMC and MC solutions are approximately neutral The best result for preserving alkaline reserve after ageing was obtained for the paper samples subjected to triple mixture with CMC/MC ratio 50/50.

After thermal ageing, relatively better preservation of alkaline reserves of papers treated with triple mixture having CMC/MC ratio of 50/50 compared to that of the papers treated with triple mixtures having CMC/MC ratios of 25/75 and 75/25 is a result of synergistic effect of MC and CMC mixture.

Experimental data on the examination of the effect of CMC/MC ratio on surface pH was shown in Figure 6. Triple mixtures containing different ratios of CMC/MC increased the surface pH values of papers from 6.6 to around 9 in general.

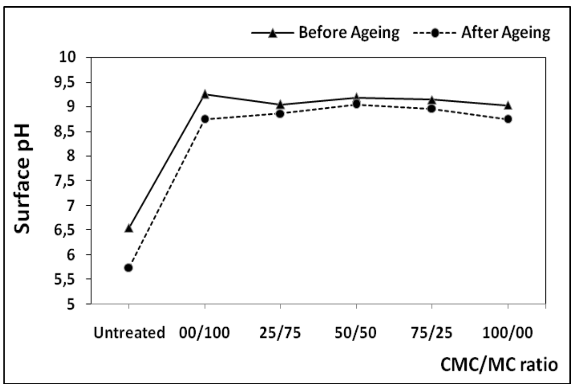

Figure 6. Effect of CMC/MC ratio in triple mixture on surface pH of paper.

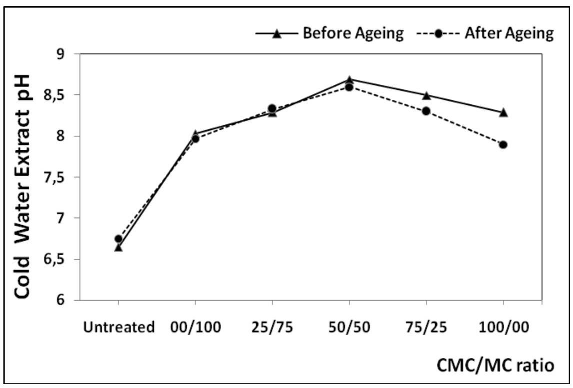

Figure 7. Effect of CMC/MC ratio in triple mixture on cold water extract pH of paper.

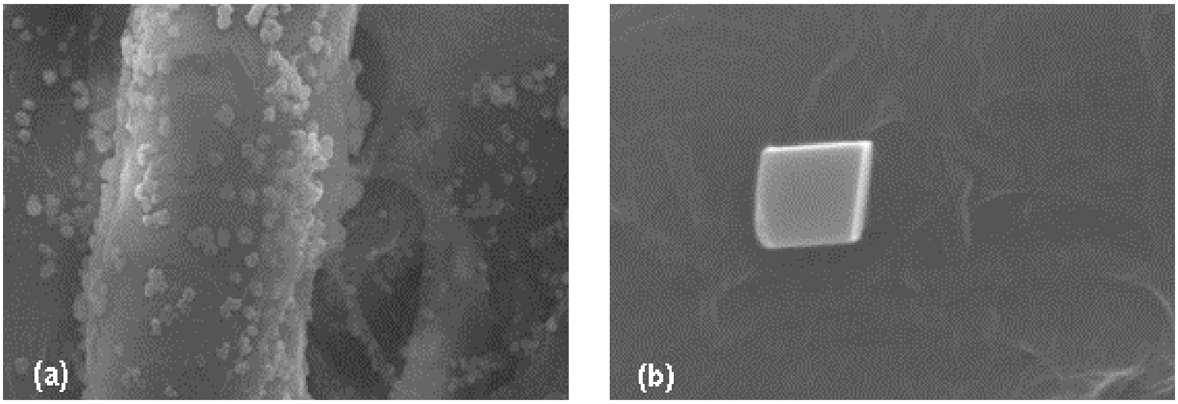

Figure 8. $Ca(OH)_2$ particles on the surface of paper treated with triple mixture containing 1-1-1 % MC-CMC-$Ca(OH)_2$.

The resistance of surface pH of paper samples treated with triple mixtures against ageing is better than that of the untreated samples, and the best surface pH resistance was obtained for the paper sample treated with triple mixture having CMC/MC ratio of 50/50.

It was observed that triple mixture with a CMC/MC ratio of 50/50 stabilized paper against acidic hydrolyis to a higher extent than the other mixtures (Figure 7).

Determination of a suitable calcium hydroxide concentration in triple mixture

Size distribution values obtained for aqueous dispersion of $Ca(OH)_2$ prepared for being used in triple mixture are as follow: d(0.1): 0.974 μm, d(0.5): 2.412 μm and d(0.9): 10.045 μm.

According to these values, the particle sizes are in micron level. However, it was clearly seen from the SEM photographs (Figure 8a) of $Ca(OH)_2$ particles on paper surface treated with triple mixture that sizes of most of the particles are under 1 μm, at nano sizes. This result indicates that $Ca(OH)_2$ particles are mostly in coagulated form in aqueous suspension. It can be concluded from the examination of $Ca(OH)_2$ crystals on paper surface in Figure 8a and single $Ca(OH)_2$ crystal in Figure 8b that, $Ca(OH)_2$ particles crystallized in disturbed cubic crystal form under our synthesis conditions.

In media in which cellulose ethers such as MC and CMC are present, $Ca(OH)_2$ causes to combination of these molecules by leading to dipole interactions among them. As a result of this effect, gel formation which cannot be prevented by mixing is observed when $Ca(OH)_2$ is added in solid form or in suspension into MC-CMC solutions. Gelling was prevented by adding the components into mixture in the order of $Ca(OH)_2$-MC-CMC.

Concentration of $Ca(OH)_2$ in triple mixtures was changed in the range of 0.25% - 2%, by keeping

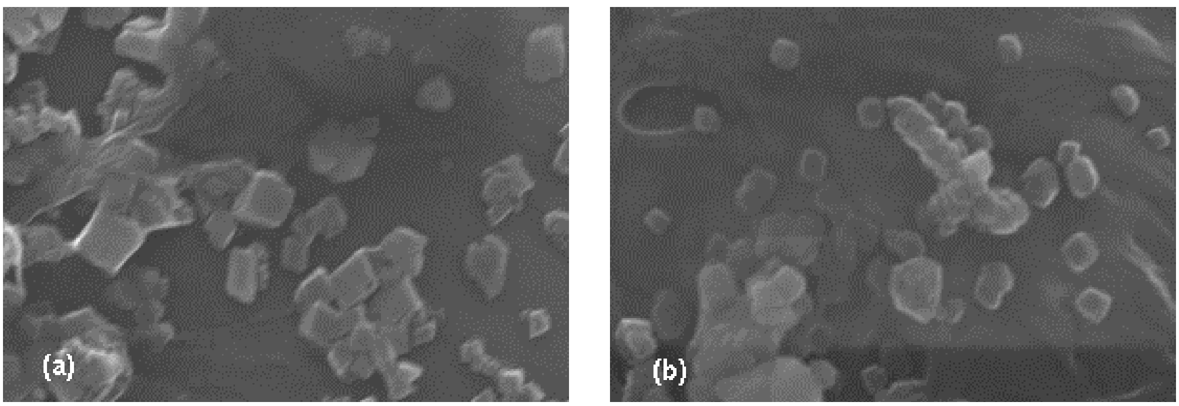

Figure 9. SEM images of paper samples treated with triple mixture containing 1-1-2% MC-CMC-$Ca(OH)_2$ before (a) and after (b) ageing.

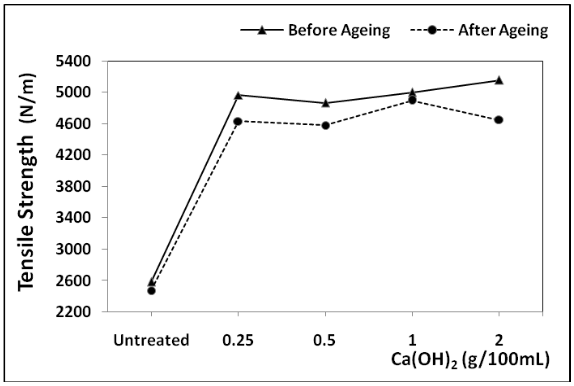

Figure 10. Effect of $Ca(OH)_2$ concentration in triple mixture on tensile strength of paper.

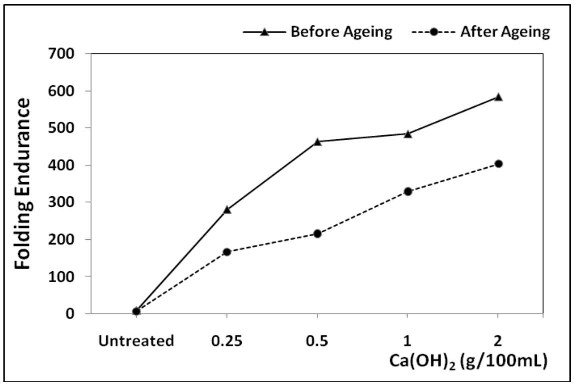

Figure 11. Effect of $Ca(OH)_2$ concentration in triple mixture on folding endurance of paper.

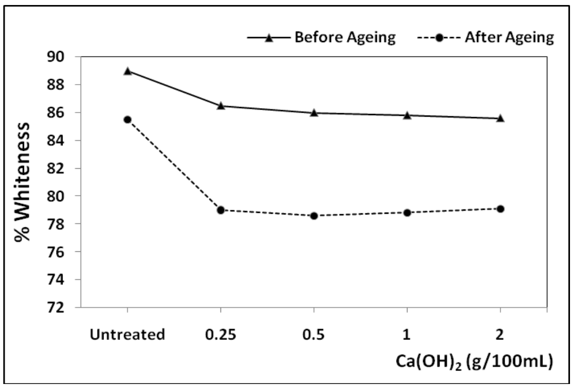

Figure 12. Effect of $Ca(OH)_2$ concentration in triple mixture on whiteness of paper.

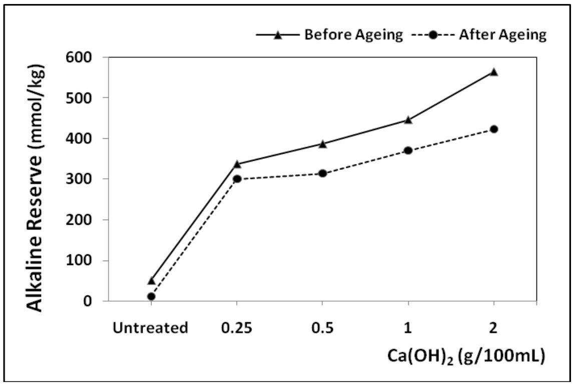

Figure 13. Effect of $Ca(OH)_2$ concentration in triple mixture on alkaline reserve of paper.

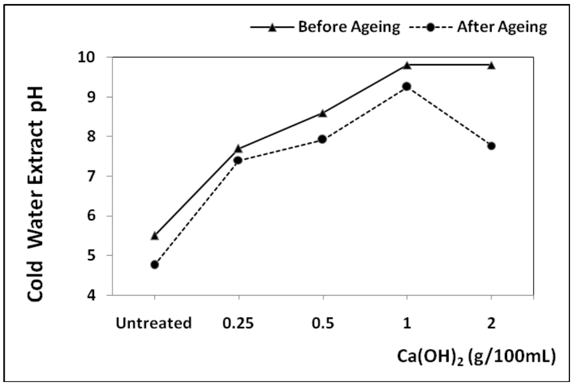

Figure 14. Effect of $Ca(OH)_2$ concentration in triple mixture on cold water extract pH of paper.

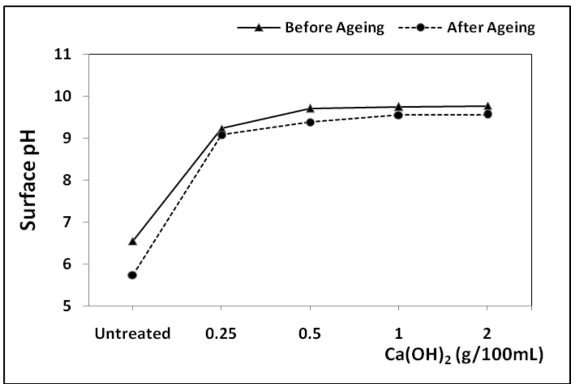

Figure 15. Effect of $Ca(OH)_2$ concentration in triple mixture on surface pH of paper.

CMC/MC ratio constant at 50/50. SEM images of papers treated with triple mixture containing the highest $Ca(OH)_2$ concentration (2 %), before and after accelerated ageing are shown in Figure 9. It was observed that, relatively small particles were left on paper surface and bigger particles were removed after ageing. It was also observed that, smooth borders of $Ca(OH)_2$ crystals (Figure 9a) were partly deformed (Figure 9b) after ageing depending on the chemical effects during ageing process.

Changing $Ca(OH)_2$ concentration in triple mixtures in the range of 0.25% - 2% by keeping CMC/MC ratio constant at 50/50 increased the tensile strength of papers approximately 2 folds, independent of $Ca(OH)_2$ concentration (Figure 10). Folding endurance of paper samples increased linearly proportional to $Ca(OH)_2$ concentration (Figure 11). Similar effects of $Ca(OH)_2$ on tensile strength and folding endurance of papers were also reported by other researchers [31,32]. It was concluded from Figure 12 in which whiteness values of paper samples treated with triple mixtures having different $Ca(OH)_2$ concentrations before and after ageing were given that, the whiteness of papers were not affected considerably by $Ca(OH)_2$ concentrations of triple mixtures. Due to the character of $Ca(OH)_2$, alkaline reserves of papers increase with increasing $Ca(OH)_2$ concentration inherently (Figure 13).

Alkaline reserves of the papers treated with triple mixture containing 1% $Ca(OH)_2$ was slightly over 400 mmol/kg which was accepted ideal value for papers [21] and they were preserved after ageing. Alkaline reserves of the papers treated with triple mixture containing 2% $Ca(OH)_2$ increased up to 565 mmol/kg, and decreased much more than that of other papers after thermal ageing (Figure 13). This decrease originates from acidic products formed by alkaline hydrolysis of cellulose. Similarly, pH value of aqueous extract of papers treated with triple mixture containing 2% $Ca(OH)_2$ after thermal ageing decreased considerably (Figure 14).

The results given in Figure 15 were obtained from the examination of the effect of $Ca(OH)_2$ concentration of triple mixtures on surface pH of papers. All the mixtures containing different amounts of $Ca(OH)_2$ increased the surface pH of Whatman filter paper from 6.5 to around 9.5. Remaining the surface pH value at around 9.5 although the increasing alkaline reserve and pH of aqueous extract of paper with increasing concentration of $Ca(OH)_2$ in triple mixture was concluded as the result of restricted diffusion of triple mixture into paper.

The results obtained in this study showed that mechanical properties of paper were improved by using CMC/MC mixtures instead of only pure CMC or MC. For example, it was observed that triple mixtures containing different ratios of CMC/MC and $Ca(OH)_2$ increased tensile strength of papers approximately 2 folds and synergistic effect of CMC and MC mixture increased the tensile strength much more. Triple mixtures also increased the folding endurance of paper samples considerably.

$Ca(OH)_2$ particles used for the preparation of triple mixtures could be synthesized at nano sizes. Improvement of mechanical properties of paper increased with increasing ratio of nano $Ca(OH)_2$ particles, but ideal concentration of an alkaline reserve was obtained with the triple mixture containing 1% (w/v) $Ca(OH)_2$. It was determined that triple mixtures containing higher ratios of $Ca(OH)_2$ caused alkaline hydrolysis of cellulose (Figures 13-14).

The most suitable CMC/MC ratio and $Ca(OH)_2$ concentration in triple mixture were found as 50/50 and 1 g/100 mL respectively. It was shown that the triple mixture containing 1% (w/v) MC, 1% (w/v) CMC and 1% (w/v) nano-micro calcium hydroxide particles deposited an alkaline reserve of 447 mmol/ kg and increased the tensile strength of Whatman No:1 filter paper from 2583 N/m to 4997 N/m and folding endurance from 281 to 484 folds.

ACKNOWLEDGEMENT

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