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Paper deacidification with the use of magnesium oxide nanoparticles

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Abstract: *Paper deacidification with the use of magnesium oxide nanoparticles.* The aim of this work was to find the differences between deacidification of paper with the use of magnesium oxide nanopowder and conventional reagent with micro-sized particles. The pH measurement of deacidified paper and scaning electron microscopy with SE, BSE and EDX detectors were applied in the study. The results proved that magnesium oxide washing increases pH of paper more efficiently than conventional reagent. Magnesium oxide nanopowder was also shown to deposit a significant amount of alkaline reserve.

Keywords: paper conservation, deacidification, magnesium oxide, nanoparticles, SEM –SE, BSE, EDX

INTRODUCTION

The fact that the evolution of the papermaking processes in the mid of 19th century resulted in paper of poorer durability is not questionable. The use of wood pulp that is more reactive then white cottons or linen rags and introduction of acid substances during paper sizing have reduced the chemical resistance of paper. Acid-catalyzed hydrolysis of cellulose became the most important source of paper degradation (Baty et al. 2010). In order to prolong paper life many methods of neutralizing acids within the paper and to create an alkaline buffer have been elaborated. Deacidification treatments are either aqueous or non-aqueous. Non-aqueous processes should be used when paper is sensitive to water or contain water-soluble inks and dyes. Among the non-aqueous methods the most important are the Wei'tO and Bookeeper

(Gorgi et al. 2005). The latter my be used as single items technique and for mass deacidification. The Bookeeper method (MgO in an inert carrier) applied in spray presents some disadvantages like color changes after aging (Stauderman et al. 1996) and whitening of paper (Kozielec 2009). Another problem is the size of the MgO particles that hinders their penetration inside the paper structure, and thus limits the effectiveness of deacidification. These limitations of the efficiency of deacidification, connected with the dimensions of the deacidifier's particles encouraged us to search for their potential reduction using the suspension MgO nanoparticles in 2-propanol.

MATERIAL

Nanoparticles (p.f.a., 99,8 % trace metal basis, Aldrich, No 549649), with particles <50 nm (BET analysis) were used as an deacidifying reagent. For comparative purposes paper samples were also deacidified with the use of simple MgO (p.f.a. POCh Gliwice).
Model blotting paper - Whatman 3Chr MM (grammage 180 g/m^2) – was used in the test. The initial pH level of the blotting paper (cold water) amounted to 7.36. Samples of 4 $\times$ 4 cm were cut out of the Whatman paper. They were then acidified in H_2SO_4 solution until they reached the reaction of pH 3.8 - 5.3. After establishing the humidity both samples were deacidified in a bath (2×0.5 h) and with the use of a dispersion of MgO nanoparticles or conventional MgO reagent in 2-propanol (p.f.a, Honeywell). The samples were then subjected to analysis after 10 days since the process of deacidification was completed (in order for $MgCO_3$ to be produced as a result of CO_2 absorption from the air – alkaline reserve).

METHODS

The effectiveness of acidification and deacidification of the paper samples was controlled while analyzing the pH of water extract (Tappi T 509 om-02). The samples were observed under a scanning electron microscope (SEM) by LEO Electron Microscopy 1430 VP. The samples were analysed under the microscope as both – sputtered and unsputtered with Au – in case of the latter SE detector was used (Secondary Electron). In order to evaluate the decomposition of magnesium on the surface of the samples SEM was applied together with a detector of backscattered electrons BSE (Backscattered Electron), whereas quantitative analyses of magnesium on paper surface were carried out using an Energy Dispersive X-ray (EDX) spectrometer (Quantax 200) coupled with an XFlash 410 detector (BrukerAXS). The test were carried out on the Faculty of Chemistry of the Nicolaus Copernicus University in Toruń.

RESULTS AND DISCUSSION

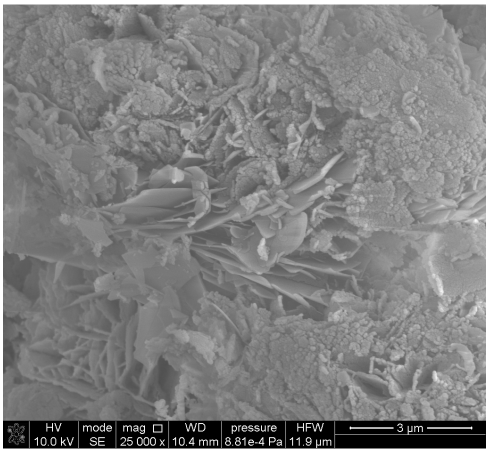
The tests included the comparison of the effects of deacidification with a standard magnesium oxide with particles of a micrometric size and deacidification with the same compound but incorporated in a form of nanoparticles. The aim of the experiments was to find what is the degree of nanoparticles penetrating the structure of paper more effectively, and whether the improvement of the effectiveness of deacidification is significantly better than in case of a standard reagent. The tests were conducted in model papers, in conditions with pH similar to pH of archive papers sized with $Al_2(SO_4)_3$. Whatman paper was used in the tests which is homogenous in terms of the composition of fibrous and does not contain mass supplements, fillers, rosin sizes etc. The use of historical papers in the tests, containing different amounts of filling agents, which were very often unequally placed on the surface of a paper sheet could hinder the interpretation of the results of neutralization marks. The presence of auxiliary compounds, particles of glue, filling agents and especially magnesium compounds in historical papers as well as diversified fibrous structure of paper stuff could also hinder the microscopic observation, the examination of the composition of surface with SEM-EDX method in particular.

The differences in effectiveness of penetration, which refers to deacidification with the use of these two compounds (reagent of micro- and nano- size) are shown in Table 1. As one can see, the pH of paper after oxide processing in a form of nanoparticles was higher than in case of deacidification with its standard counterpart of micrometric size. It confirms the reports of higher reactivity – related to acids – of magnesium compounds used as a source of alkalis in a form of nanoparticles, their (i.e. acids) easier neutralization and the formation of alkaline reserve (Poggi et al. 2010). By applying dyspersion with concentration of 0.025% indeed pH of water extract was obtained with the pH level of 9.15, which can be seen as a satisfying result from the point of view of conservators' expectations (Stauderman et al. 1996), however the possibility of adaptation of the concentration of deacidifier to conservation requirements is significant. It needs to be emphasized that for pH>8,5 the rate of oxidative reactions, catalysed by the presence of Cu ions, which increase cellulose degradation processes, is getting higher (Poggi et al. 2010).

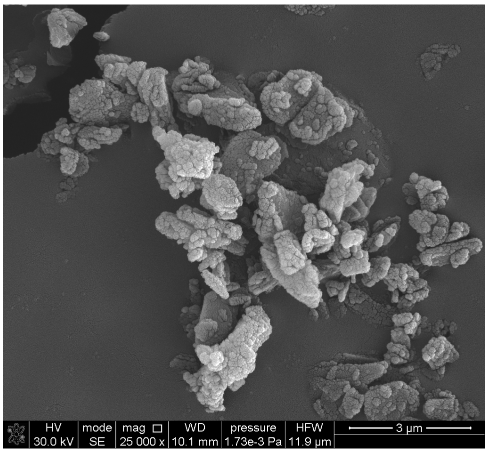
Table 1. The effectiveness of deacidification in bath with standard $Mg(OH)_2$ and nanoparticles $Mg(OH)_2$

Deacidifier	Concentration of MgO in 2-propanol [%]				
	0.0125	0.025	0.05	0.1	0.2
	pH of paper				
MgO conventional	3.68	3.95	4.64	4.7	8.95
MgO nanopowder	6.25	9.15	10.09	10.27	-

Microscopic analyses (SEM-SE) showed differences in sizes of particles between conventional MgO and a reagent of a nanometric size (Figures 1a and 1b). The particles of two different reagents (conventional one and that of a nanometric size) differed also in shape. Nanoparticles associated into agglomerates of rhomboid-shape crystallites whereas conventional MgO associated into agglomerates of different shapes and forms including flakes. Preliminary observations of paper samples after they had been deacidified with SEM-BSE methods (Figures 2a and 2b) and SEM-EDX methods (Figures 3a and 3b) showed some differences in the spatial organization of the particles of conventional MgO and that of a nanometric size. They also confirmed the differences in sizes of the particles of both of the reagents – the particles of conventional MgO are considerably larger than the agglomerates of MgO nanopowder. Quantitative determinations of magnesium surface distribution using SEM-EDX method showed higher Mg content in paper treated with MgO nanopowder than in the case of conventional reagent.

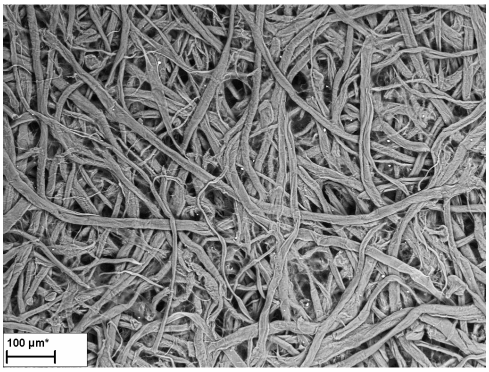


a

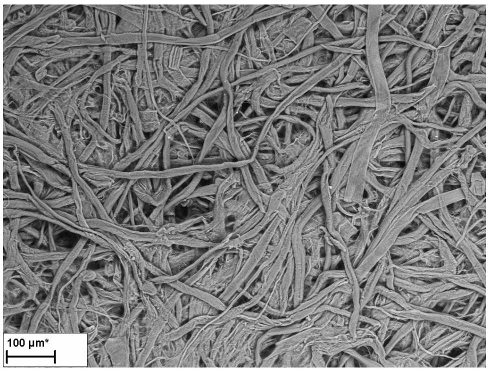


b

Figure.1 SEM-SE images of conventional MgO agglomerates (a) and nanopowder (b).



a



b

Figure 2 SEM-BSE images of Whatman paper after using conventional magnesium oxide (a) and nanoparticles of MgO (b) for paper deacidification.

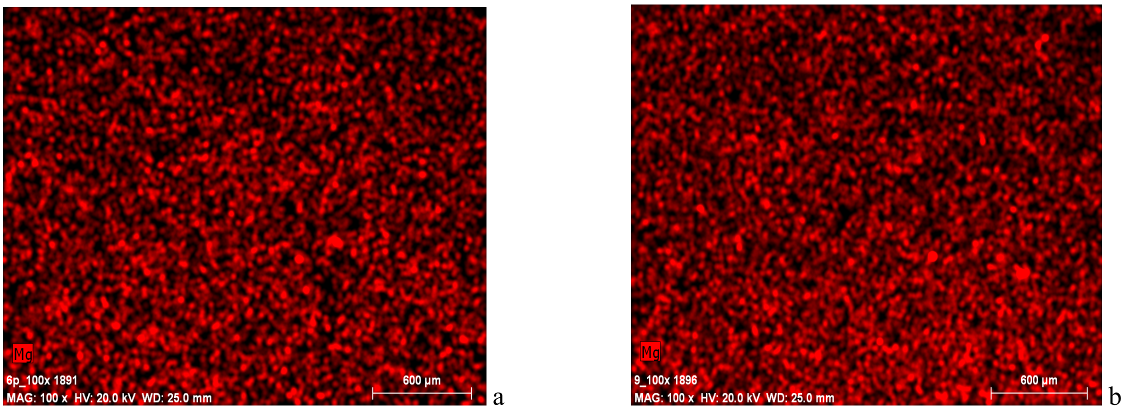


Figure 3. SEM-EDX images of Whatman paper after using conventional magnesium oxide (a) and nanoparticles of MgO (b) for paper deacidification.

CONCLUSION

Magnesium oxide nanoparticles tend to deacidify paper more effectively than the same reagent but with particles of a micrometric size. Preliminary tests conducted with scanning microscopy methods (SEM -BSE and SEM-EDX) showed differences in the spatial organization of particles on the surface of paper. Quantitative determination of magnesium on the surface of samples conducted with SEM-EDX method showed higher Mg content in case of paper treated with nanoparticles than in case of the sample treated with standard MgO of a micrometric size. The increase of the pH of paper after deacidification with MgO nanoparticles is to be associated with better penetration of the reagent into the structure of paper.

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Streszczenie: *Odkwaszanie papieru nanocząstkami tlenku magnezu.* Celem pracy było porównanie efektywności odkwaszania papieru tlenkiem magnezu o mikrometrycznych i nanometrycznych rozmiarach cząsteczek. Analizy pH oraz SEM-EDX papierów po odkwaszaniu o wykazały, że nanocząsteczki MgO efektywniej odkwaszają papier niż konwencjonalny reagent o mikrometrycznych wielkościach cząsteczek.

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