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Rapid synthesis of antimicrobial paper under microwave irradiation

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ABSTRACT

The silver-nanoparticle (AgNP) containing paper was successfully prepared. The AgNP is deposited by the in situ reduction of silver nitrate on the acrylamide grafted bagasse paper sheets in the presence of citrate molecules as stabilizing agent. In the present paper, grafting of acrylamide onto bagasse paper sheets using potassium persulfate was carried out under the influence of microwave radiations (MWR). The modified paper sheets were characterized by Fourier transform infrared spectroscopy (FTIR), UV-spectroscopy, and scanning electron microscopy (SEM). Antimicrobial activities of the prepared paper sheets were also investigated against G+ve bacterium *Staphylococcus aureus*, G−ve bacterium *Pseudomomas aeruginosa*, and yeast *Candida albicans*, which are model microorganisms for testing bactericidal properties. The AgNP containing paper sheets exhibited antibacterial activity.

1. Introduction

Recently, the need of developing materials based on renewable and/or biodegradable resources has known a growing interest (Belgacem & Gandini, 2008; Sabu & Pothan, 2008; Wool & Sun, 2005), because bio-based materials could be a promising solution both in terms of environmental and performances aspects (Hafren & Cordova, 2005). In addition the hybridization of the natural polymers with synthetic polymers yields new material, which could have desirable properties including biodegradability (Balbir, Rajeev, Asim, & Mithu, 2009). There are many techniques to do this hybridization; one of these techniques is the grafting of monomer into cellulose. The conventional technique of grafting and chemical modification of natural fibers requires significant time and energy (Susheel, Sunil, & Kaith, 2009). Microwave radiation (MWR) is a potentially attractive technique as it provides a volumetric heating process at improved heating efficiencies as compared with conventional techniques (Appleton, Colder, Kingman, Lowndes, & Read, 2005).

Microwave technology uses electromagnetic waves, which passes through material and causes its molecules to oscillate. It is not observed by non polar materials to any degree while polar water molecules held within a polymer matrix do absorb energy very proficiently, thus becoming heated (Kaith & Kalia, 2008). It has been observed that monomers with polar groups favor the absorption of microwave radiations. Grafting under MWR has advantages in terms of time consumption and cost effectiveness as well as reduces the extent of physico–chemical stresses to which the fibers are exposed during the conventional techniques. It was found that properties of fibers treated under MWR are same or even better than those of fibers modified through other conventional techniques (Kaith & Kalia, 2008). Currently the graft copolymerization has been successfully conducted under MWR. There are few literature reports about microwave-assisted rapid synthesis of graft copolymers of cellulose in aqueous medium. So, the present research work is focused on the graft copolymerization of acrylamide (AM) onto bagasse paper sheets using MWR. Grafting of methyl methacrylate onto acetylated *Saccharum spontaneum* L. fiber using ferrous ammonium sulphate–potassium per sulphate (FAS–KPS) redox initiator under the influence of MWR has been reported (Balbir et al., 2009). Also, the graft copolymerization of methyl methacrylate onto bamboo cellulose was successfully conducted by MWR (Zhenglong et al., 2011). Grafting of polyaniline onto gum acacia (Tiwari & Singh, 2006) and grafting of acrylic acid onto chitosan (Ge, Wan, & Luo, 2006) have involved the use of MWR. Polyacrylamide was graft copolymerized onto chitosan using MWR and maximum grafting 169% was observed in 1.16 min, under optimum reaction conditions (Singh, Tiwari, Tripathi, & Sanghi, 2006). Grafting of binary mixtures consisting of methyl methacrylate with ethyl acrylate, acrylonitrile, acrylic acid, vinylacetate, acrylamide and styrene using ferrous ammonium sulphate under the influence of MWR was carried out by Susheel et al. (2009).

Nanomaterials with unique electronic, optical and catalytic properties have recently been at the forefront of research due to their tremendous range of applications. The functionalization of paper with only a very small concentration of nanoparticles is

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able to produce devices with excellent photocatalytic, antibacterial, anti-counterfeiting, surface enhanced Raman scattering and surface plasmon resonance performances (Ying, Dan, George, & Gil, 2011).

Compared with other metals, AgNP have been widely used in a range of bactericidal applications due to their broad-spectrum antimicrobial activities and high toxicity to different type of microorganisms (Nassar & Youssef, 2012; Morones et al., 2005). The antimicrobial properties of AgNP are believed to be size dependent, where smaller AgNP, with larger surface areas accessible for interaction provide more antimicrobial effect than larger AgNP (Sharma, Yngard, & Lin, 2009). In this case, aggregation of AgNP on the paper structure must be avoided to produce an efficient antimicrobial paper. The potential toxicity of AgNP to human is still a matter of considerable debate. Hence, strong binding forces between AgNP and paper substrate are desirable to reduce possible exposure. Fernández et al. (2009) studied cellulose substrates as holders of AgNP to form a cellulose-AgNP hybrid material in order to preserve aseptic conditions in an absorbent pad. Tankhiwale and Bajpai (2009) developed AgNP-loaded filter papers with excellent antimicrobial properties against *Escherichia coli*. The degradable nature of paper makes it an attractive alternative for antibacterial food-packaging material, as a replacement for synthetic polymeric films.

Here, a simple method to develop coating of AgNP on paper is presented, and the coatings are characterized using Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Antibacterial activities of the prepared paper sheet were also investigated against Candid, Pseudomona, *Staphylococcus aureus* which are the model microorganisms for testing bactericidal properties.

2. Experimental

Unbleached Kraft pulp was kindly provided by IDFO Company, Egypt. Acrylamide (AM) potassium persulfate (ALPHA CHEMIKA) were used without further purification. Silver nitrate ($AgNO_3$) (SISCO Research Laboratories Pvt., Ltd., India) and trisodium citrate $C_6H_5O_7Na_3$ (Sigma–Aldrich, UK) of analytical grade purity, were used without further purification.

2.1. Preparation of paper sheets

The paper sheets were prepared according to the S.C.A standard, using the model S.C.A sheet former (AB Worentzen and Wettre). In the apparatus a sheet of 165 mm diameter and 214 cm^2 surface area was formed. The weight of oven dry pulp used for every sheet was about 1.8 g. After sheet formation, the sheet was pressed for 4 min using a hydraulic press. Drying of the test sheets was made with the help of a rotating cylinder or drum at $60 \pm 5\,^{\circ}C$ for 2 h.

2.2. Graft copolymerization synthesis

A known amount of bagasse paper sheet was immersed in a definite amount of distilled water for 24 h prior to graft copolymerization synthesis in order to activate the reactive sites on the surface. A known amount of initiator potassium persulfate (KPS) and monomer (AM) was then added to the flask containing paper sheet. The reaction flask containing the reaction mixture was placed in a microwave for 30 s.

The grafted paper was treated with acetone, and washed with mixture of methanol:water (80:20) mixture to remove the unreacted monomer and reagent followed by drying in vacuum oven at $40\,^{\circ}C$ to a constant weight.

2.3. Loading of silver nanoparticles into grafted paper sheets (GP)

The AgNP were loaded into the grafted paper sheet by using the following method; the grafted paper sheet was put in $AgNO_3$ solution (15 mg $AgNO_3$ in 40 ml distilled water) for 12 h, then was taken out and put in tri-sodium citrate solution (20 mg dissolved in 25 ml water) for next 12 h to reduce Ag^+ ions into AgNP. The material, so produced, was allowed to dry. In this way, AgNP loaded grafted paper sheet was prepared.

2.4. Characterizations

2.4.1. Infrared (IR) spectral analysis

FTIR spectra of non-grafted bagasse paper sheet, grafted bagasse paper sheets, and AgNP containing paper sheets were recorded in the range of 400–4000 cm^{-1} on (Shimadzu 8400S) FTIR Spectrophotometer.

2.4.2. Scanning electron microscopy (SEM)

The surface morphology of non-grafted bagasse paper sheets, grafted bagasse paper sheets, and AgNP containing paper sheets was analyzed using electron microscope FEI INSPECTS Company, Philips, Holland, environmental scanning without coating.

2.4.3. UV-spectroscopy

UV-spectroscopy was carried by Shimadzu-Recording Spectrophotometer UV-240. The spectrum of the sample was recorded in the wavelength range of 300–800 nm.

2.4.4. Assay of antibacterial activity

The disc diffusion method was used to determine the antimicrobial activity of the prepared paper sheets. A volume of 0.1 ml of the tested microorganisms grown in Brian Heart Infusion Broth (at $42\,^{\circ}C$ for 24 h, 108–109 cells/ml), was inoculated on Brian Heart Infusion media, and then spread on the entire surface of the dish using a sterile spatula. Subsequently, sterile discs were placed onto agar at certain intervals by passing gently. After the plates were incubated at $42\,^{\circ}C$ for 24 h, the inhibition zones around the discs where no growth occurred, were measured in millimeters, the experiments were repeated in duplicated for all of the test strains.

3. Results and discussion

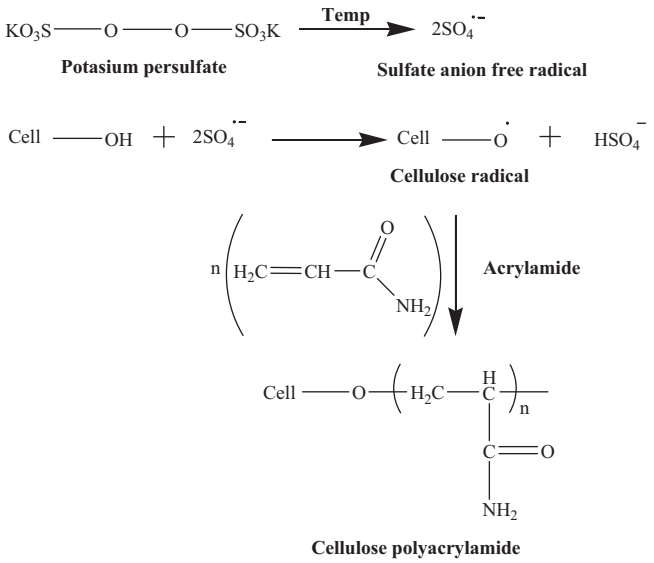
3.1. Mechanism of grafting and loading AgNPs

Graft copolymerization of vinyl monomers onto cellulose has been studied extensively (Chen & Hsieh, 2005; Sabaa & Mokhtar, 2002; Salam, 2005; Samir, Hassan, & El-Sakhawy, 2006; Samir, Ibrahim, & Sher, 2009; Samir, 2000; Zahran & Mahmoud, 2003). C_2, C_3, and C_6–OH groups and C–H_2 sites are the active centers for grafting of monomer chains onto cellulosic biopolymers. Indeed, the mechanism of grafting reaction is more or less the same for different cellulosic materials and may briefly be given in Scheme 1.

The silver colloid was prepared by using chemical reduction method according to the description of (Lee, Shin, Kim, & Oh, 2004).

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^- + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2 \uparrow$$

The overall process of entrapment of nano silver can be explained according to Rasika and Bajpai (2009) as follows: when grafted paper sheet is equilibrated in distilled water, the network swells due to hydrophilic nature of monomer and plasticization of macromolecular chains. On dipping swollen paper into aqueous solution of $AgNO_3$, Ag^+ ions enter into the swollen grafted network. Later on when this Ag^+ containing paper sheet is put in the sodium citrate solution, a uniformly distributed array of AgNP is



Scheme 1. Proposed mechanistic pathway for the synthesis of PAM-g-cellulose copolymer.

obtained due to reduction of Ag^+ ions. The crosslinked three dimensional networks serve as stabilizer for AgNP and prevent them from aggregation.

In our work, similar hydrogen bonding was achieved between citrate molecules attached to AgNP and amide moieties of the coated layer of paper sheet. Thus, the added citrate (or citric acid), stabilized and assembled AgNP on the cross-linked polyacrylamide.

At the end of the reaction, the colorless aqueous solutions of formulations containing $AgNO_3$ turned to fully brown–yellow solid. The difference between colors of paper sheets without and with AgNP is shown in Fig. 1, which clearly describes the color change observed due to reduction of Ag^+ ions into AgNP. It is very clear that paper sheet brown due to presence of AgNP.

3.2. FTIR spectra

Fig. 2 presents the FTIR spectra of grafted paper sheet and Ag-loaded paper sheet samples. The spectral profiles do not allow more detailed analysis of any changes of the Ag-clusters. The main evidence by the FT-IR experiments in Fig. 2 is that the small clusters of Ag formed do not modify the sheet surface. Also, the small amount of Ag and the fact that the Ag-clusters have very small absorption coefficients makes them difficult to detect by IR-spectroscopy.

IR spectra has shown absorption peaks at 1664 cm^{-1} relating to amide and C=O stretching. The peak observed at 1454 cm^{-1} is due to CH_2 bending, and the peak at 2933 cm^{-1} is characteristic of $-CH_2$ asymmetric stretching. In addition, the stretching vibration at 3475

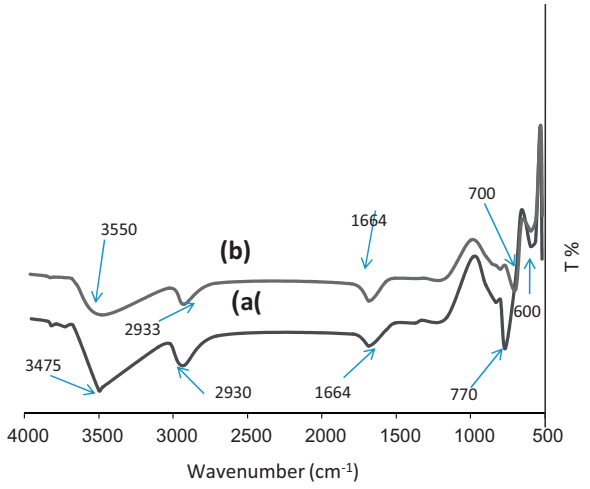


Fig. 2. FT-IR spectra of grafted paper sheet (a) and Ag-loaded paper sheet (b).

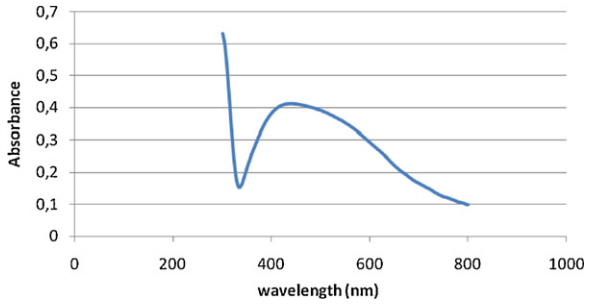


Fig. 3. UV–vis absorption spectra of colloid solution of Ag nanoparticles.

corresponding to OH/NH_2 groups has shifted to 3550 cm^{-1}, indicating that the silver particles are bounded to the functional groups present both in cellulose and amide. The shifting of the peak is due to formation of coordination bond between the silver atom and the electron rich groups (oxygen/nitrogen) present in grafted sheet. This causes an increase in bond length and frequency (Kanikireddy et al., 2011).

3.3. UV-spectroscopy

The AgNPs characterizes using UV–vis spectroscopy which shows an absorption band around 420 nm confirming the formation of nanoparticles (Hemant, Narendra, Narayan, Dushyant, & Ganesh, 2012). The dispersions of silver nanoparticles display intense colors due to the plasmon resonance absorption (Fig. 1). The surface of a metal is like plasma, having free electrons in the conduction band and positively charged nuclei. Electrons are

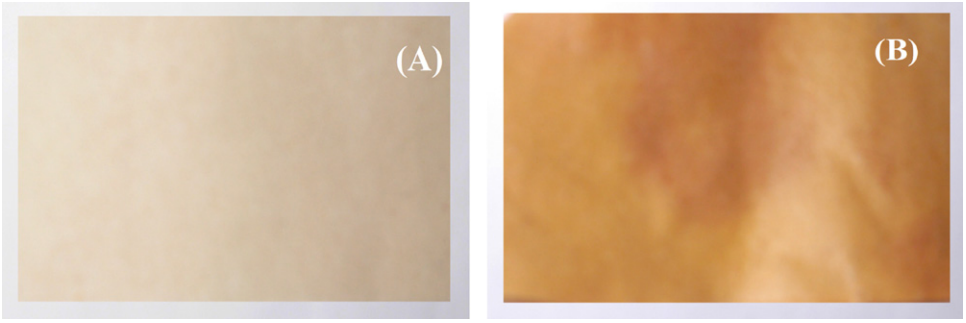


Fig. 1. Photographs of the prepared paper sheets without (A) or with (B) Ag NPs.

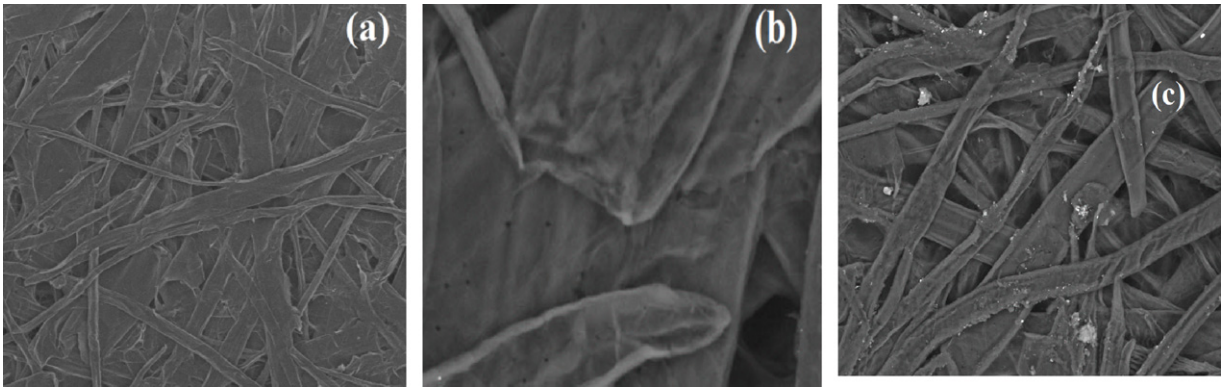


Fig. 4. Untreated paper sheet (a), graft paper sheet (b), and AgNPs containing paper sheet (c).

limited to specific vibrations modes by the particle's size and shape. Therefore, metal-like nanoparticles have characteristic optical absorption spectra in the UV–vis region (Kulkarni, 2009).

The UV–vis absorption spectrum of silver nanoparticle is shown in Fig. 3. One can clearly see absorption exhibited around 400–420 nm, which is a typical plasmon band, confirming the formation of silver nanoparticles.

3.4. Characterization by SEM

Morphological studies of paper sheet, grafted paper sheet, and AgNP doped grafted paper sheets were performed by scanning electron microscopy (Fig. 4) which reveals a clear-cut distinction between the scanning electron micrographs (SEM) of original paper sheet (Fig. 4a), graft paper sheet (Fig. 4b), and AgNP containing

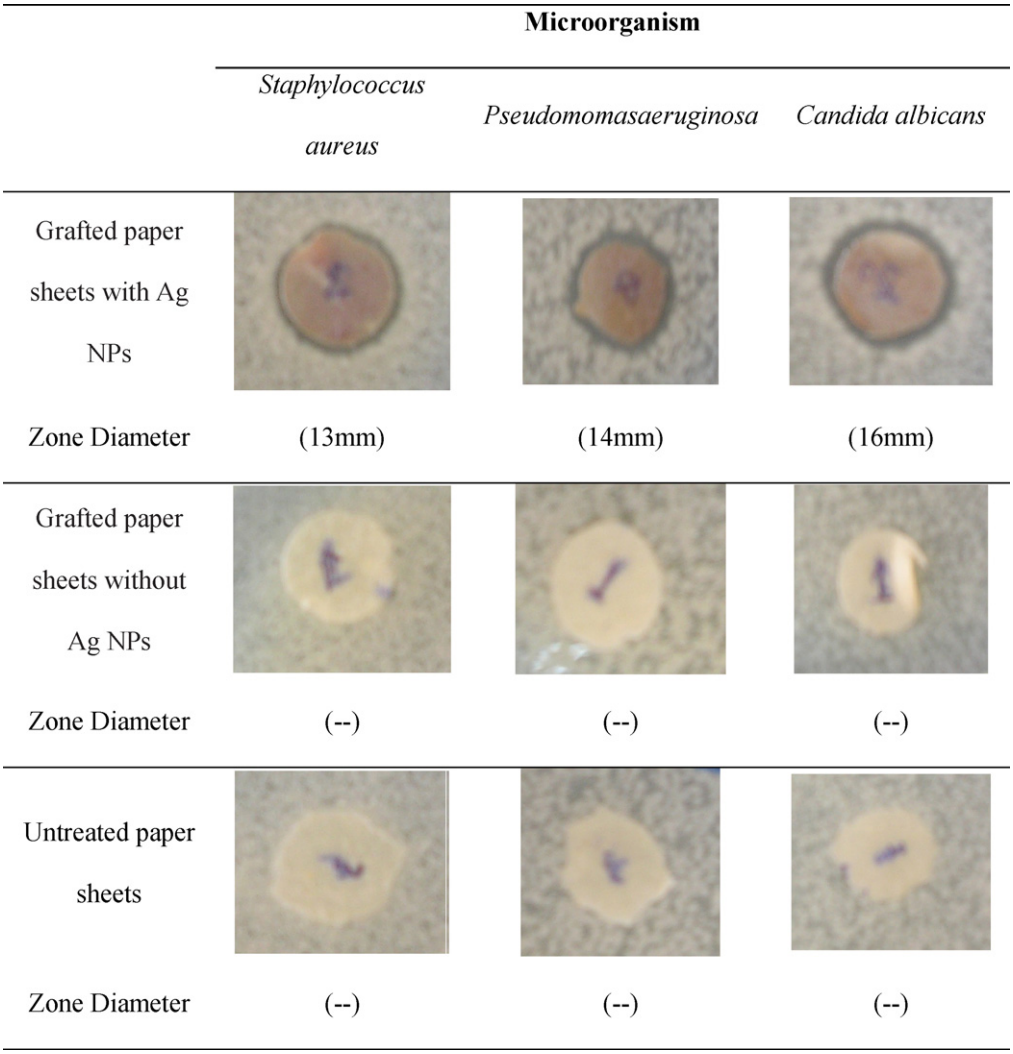


Fig. 5. Anti-bacterial activity of the paper sheet with or without Ag NPs against G+ve bacterium *Staphylococcus aureus*, G−ve bacterium *Pseudomomas aeruginosa*, and yeast *Candida albicans*.

paper sheet (Fig. 4c). The smoothness and evenness of the cellulose surface were observed in the micrograph of original paper sheet. The unevenness of surface resulted from deposition of polymer, which formed during graft copolymerization with AM or AgNP. There was a sufficient deposition of PAM onto paper sheet (Fig. 4b). It can be observed that the surface of the grafted cellulosic is extremely rough in comparison with the ungrafted fibers, which is attributed to the high graft density.

3.5. Antibacterial activities of the paper sheets

AgNP are being considered as a nontoxic environmentally friendly antibacterial material. Recent advances are aimed to discover promising paths to prepare AgNP containing paper sheets. Antibacterial effect of the paper sheets with and/or without AgNP was obvious as shown in Fig. 5. As can be seen from the size of inhibition zones, this effect was found to be more pronounced against yeast *Candida albicans* (16 mm) than gram-positive bacterium *S. aureus* (13 mm), gram-negative bacterium *Pseudomomas aeruginosa* (14 mm). It was noticed that higher inhibition zone sizes against all strains were observed with AgNP containing paper sheet with in contrast to untreated and grafted paper sheets without AgNP which did not exhibit any antibacterial activity.

4. Conclusion

From this study it may be concluded that, silver ions were stabilized via their electrostatic interactions with the electron-rich nitrogen atoms in the polyacrylamide grafted bagasse paper sheet, thus enabling them to be reduced at room temperature and be tightly anchored to the grafted bagasse paper sheet. So, the grafting of AM onto bagasse paper sheet, followed by incorporation of AgNP results in development of a novel biomaterial which demonstrates fair biocidal action against G+ve bacterium *Staphylococcus* aureus, G−ve bacterium *P. aeruginosa*, and yeast *C. albicans*, and it can be used as an antibacterial packaging material to prevent food stuff from bacterial infection. Since the used method does not involve organic solvents or harsh conditions, this method can be applied for the manufacture of antibacterial food packaging material.

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